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300-kilocycle ultrasonic emulsification of paraffin oil in distilled water

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300-KILOCYCLE ULTRASONIC EMULSIFICATION OF PARAFFIN OIL IN DISTILLED WATER

by

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

Emulsions have been in existence for thousands of years in the form of cosmetics, food, and medicines. Emulsions cover a vast number of products in both household and industrial use. Homogenized milk, butter, mayonnasise, salad dressing, and sauces are emulsions that are used every day at the dinner table. Medical salves, ointments, cosmetic creams and many other pharmaceuticals are used every day by members of both sexes in the human race. Waxes and polishes for automobiles, metal, floors, leathers, and furniture are emulsions. All of the new so called "wonder paints" and "rubber-base paints" are nothing more than an emulsion of a latex dispersed in a water medium.

"Oil and water won't mix." This is an old proverb that probably has been changed by modern science. Although oil and water are immiscible with each other, it is a well-known fact that under certain conditions, a completely stable mixture can be formed from oil and water. Three things are needed to make a simple emulsion: (1) two immiscible liquids, (2) an emulsifying agent, and (3) energy to disperse one immiscible liquid in the other.

In general there are two types of emulsions: (1) oil dispersed in water and (2) water dispersed in oil. In order to obtain a fine division of the dispersed liquid,

some type of energy must be applied. The energy that is necessary to produce emulsification may come from several mechanical sources, such as agitators and colloid mills, or it may come from the mechanical energy produced through ultrasonically-induced cavitation. The term ultrasonic energy is used throughout this thesis meaning energy coming from ultrasonic insonation. Also the emulsifying agent used must provide a film around each particle to prevent it from coalescing with others. Another purpose of the emulsifying agent is to lower the interfacial tension so that extremely fine drops (less than one micron) can easily be formed and have a restricted tendency to recombine.

The purpose of this investigation was: (1) to produce an oil-in-water emulsion, using a heavy white mineral oil (USP) and distilled water as the two immiscible liquids, (2) to employ ultrasonic energy generated by a piezoelectric crystal, (3) to evaluate the emulsion through the use of photomicrographs taken of each emulsion.

II LITERATURE REVIEW

The literature review includes the theory and mechanism of emulsification, basic theory of the application of ultrasonic energy to emulsification, and the factors which affect the stability of emulsions.

Emulsions

An emulsion is a dispersion of one liquid in another liquid, the two liquids being immiscible with each other. The dispersion is in the form of small droplets. In some cases, these droplets are stabilized by an electrical charge and behave like any other colloidal dispersion of the same type. However, in most cases an actual film is formed by the emulsifying agents around the globules or droplets and this keeps them from coalescing[3]. The size of these globules and the stability of the emulsion is dependent upon several things; i.e., the type and amount of the emulsifying agent, the method of dispersion and time, temperature, surface tension, density, viscosity, and the amount of the dispersed phase and others.

Definition of Emulsions. The concept of emulsions is not as clean cut as it should be. Sutheim[44] gives a representative definition which is, "Emulsions are intimate mixtures

of two immiscible liquids, one of them being dispersed in the other in the form of fine droplets".

Constituents Necessary for Emulsification. Three constituents are necessary to form an emulsion: two immiscible liquids, and a third substance which promotes the emulsification and also keeps the emulsion stable after formation. This third substance is called the emulsifying agent or emulsifier.

The Emulsion Phases. A phase is a physically distinct part of a system, which can be separated by mechanical means(45). Each liquid by itself is a one-phase system. If one liquid is dispersed in another liquid after emulsification, the emulsion is a two-phase system.

Internal and External Phase. One of the liquids will appear in the emulsion in the form of separate globules and its continuity is interrupted. This is called the "discontinuous phase" and because it is at the interior of the continuous phase it is also called the "internal phase". The other liquid, which surrounds the droplets, remains uninterrupted, or is the continuous phase. The continuous phase is therefore called the external phase.

Water and Oil Phases. In the majority of emulsions, one of the two phases consists of water, or aqueous solution of various salts or organic or colloidal sub-

stances. This phase is referred to as the water phase. The other phase, which is immiscible with the first phase, is called the oil phase. This does not mean that it actually consists of oil. Any other substance, provided that it behaves toward water like oil, can form the oil phase; for example, resins, waxes, hydrocarbon, etc. These substances are referred to as oil, because in emulsions, they act very much as the oil.

Types of Emulsions. Nothing has been said so far about the important question as to whether the oil or the water plays the role of the internal phase or the external phase. Both cases are possible. Whether the oil or the water will become the external phase depends on the prevailing condition. In other words, with any given pair of immiscible liquids, two types of emulsion can be formed. One type, in which the oil is emulsified in the water is called an oil-in-water emulsion. The other type in which the water is emulsified in the oil is called a water-in-oil emulsion.

Properties of Oil-in-water and Water-in-oil Emulsions. The general properties of an emulsion are determined mainly by the external phase. The oil-in-water emulsion has water for its external phase. Therefore, it will behave like a water system. It can be diluted with water, but cannot be diluted with oil or an oil-like liquid. It will conduct an electric current because there is a continuous layer of an aqueous

solution present. It can be colored with water soluble dyes as they will be soluble in the external phase. However, just the opposite is true of a water-in-oil emulsion where the oil is the external phase and water is the internal phase. It can be thinned down with an oil or oil-like liquid, but not with water. A water-in-oil emulsion will conduct an electric current as readily as an oil-in-water emulsion. Coloring of a water-in-oil system can be achieved with an oil soluble dye.

Dispersions. A substance is dispersed if it is more or less uniformly distributed throughout another substance, which is commonly known as the dispersion medium(46).

Degree of Dispersion. The degree of dispersion is nothing more than a classification of the size of the dispersed particles(54). This classification is divided into three groups: (1) coarse dispersions, (2) colloidal dispersions, (3) molecular dispersion. It will probably be best to define each by means of examples. If, for example, some fine chalk powder is poured into a beaker of water and agitated gently, the chalk powder will become uniformly distributed, or dispersed, in the water. This type of dispersion is called a coarse dispersion because the dispersed particles are larger than 0.1 micron, which means they are very much larger than the particles of the dispersion medium. Coarse dispersion

are unstable. If the agitation of the chalk dispersion is discontinued, the chalk powder will separate or settle out according to Stokes' Law, because the chalk powder is heavier than water. Now, if finely powdered sugar is poured into water, the sugar will readily dissolve in the water. The particles will become uniformly distributed in the water and will form what is known as a molecular dispersion, better known as molecular solution. In a molecular dispersion, the dispersed particles are less than one milli-micron; they are stable in spite of the fact that the dispersed substance, sugar in the above example, is specifically heavier than the dispersion medium, the water. Between these two types of dispersion is a third type, the particles of which are smaller than the coarse dispersed particles and larger than the molecular dispersed particle, i.e., greater than one milli-micron and less than 0.1 micron. This type of dispersion is called colloidal dispersion. An example of colloidal dispersion is a gelatin dispersion in water. The particle size of the dispersed phase is the decisive factor as to whether a substance is to be classified as being in a state of coarse, colloidal, or molecular dispersion. Table I gives some indication of the range of the particle size.

TABLE I

Dispersed Systems

Coarse Dispersions	Colloidal Dispersions	Molecular Dispersions
0.1μ	0.1μ - 1mμ	1 mμ

Increasing Degree of Dispersion

Sutheim, G. M.: "Introduction to Emulsions," p. 8. Chemical Publishing Co., Brooklyn, N. Y., (1946).

Particle Size. The particle size of emulsions is given as the size of the droplets of the internal phase. The particles in an average emulsion are not uniform in size, but are a mixture of globules of different diameters. Results from a large number of measurements of the particles varies considerably. Particles as large as 25 microns are found, whereas the lower limit is somewhere near 0.25 micron. The emulsion is considered as fine if the size of the droplets is in the neighborhood of one micron, while particle size from five to ten microns is rather coarse. In comparing these figures with the limits given before for the three types of dispersion (Table I), it can be seen that emulsions belong in the class of coarse dispersions.

Homogeneous and Heterogeneous Systems. The term homogeneous is used frequently in science and practice. Its meaning has to be confined to materials with fairly uniform properties, with regard to particle size and chemical and physical behavior. Emulsions are often described as homogeneous, referring to their properties as a whole. As a physical system, emulsions undoubtedly belong to the class of heterogeneous substances. The globules of the internal phase are a thousand or more times as large as the molecules of the external phase; and they are different in chemical and physical properties. Each one of the two phases in itself can be considered as homogeneous. But emulsions are heterogeneous systems with changes of properties at the boundaries of contact[47].

Theories of Emulsions

Emulsions of oil-in-water or of water-in-oil may be prepared by suitably choosing the emulsifying agent, which is invariably necessary in order to obtain emulsions of even moderate concentration of the dispersed phase. Such emulsions may also be inverted to systems of the opposite type by adding suitable electrolytes[17]. Any general theory of emulsions and their stability must be capable of including and explaining all the above facts. Only a few of the theories will be mentioned here.

The Surface Film Theory. The first major step toward the present accepted theorem was made in 1862 by Marcet, a physiologist[55]. Marcet outlined a new theory of emulsions that was more clear and more definite than anyone before him. In his paper, he assumed the existence of a film-like structure that surrounds and protects the globules of the internal phase. Marcet's failure to explain how the film is produced, is one of the faults of the surface film theory. He also failed to state or determine what keeps the film in position and what gives it permanence, and why and under what circumstances the film gives way when the emulsion breaks. These and numerous other unanswered questions led to the formation of the surface tension theory or, as it is more correctly called, the interfacial tension theory.

Interfacial-tension Theory. Quincke and Plateau[12] were among the first to assume the reduction of the surface tension or interfacial tension to explain the formation of emulsions. They said that a pair of immiscible liquids of high interfacial tension cannot be emulsified unless the interfacial tension is lowered by suitable methods, e.g., by the addition of a "sodium soap".

The interfacial tension theory cannot be accepted as a general explanation for the formation of emulsions. The emulsion system as a whole cannot be explained only by the reduction of the interfacial tension. The surface tension theorem does postulate the existence of a protective film around the dispersed phase. This is a factor which goes far beyond the mere reduction of the interfacial tension, and shows that the pure surface-tension theory is not capable of giving a satisfactory explanation of all properties of the emulsion system.

To try to account for the phenomena of emulsification from the interfacial tension theory or surface film theory alone would be both ridiculous and impossible. These two theories are merged into a new theory, the adsorption theory, which, for the first time, gives an acceptable explanation of emulsions.

Adsorption Theory. Donnan[57] made the following statements in a paper he published in 1899: "In view of all these observations and of my own experiments the following outline

of a theory of soap emulsions (and possibly of all emulsions) seems to be on safe grounds. The soap becomes concentrated in the surface layer between the oil and the aqueous liquid. The equilibrium can be conceived in the following way: Due to its capacity of reducing the surface tension, the soap has the tendency to concentrate at the surface, because that causes a decrease in the free energy of the system. By the accumulation at the surface the effectiveness of the active substance is greatly increased. In this way the work necessary for an enlargement of the common surface is reduced to a much lower value and thus the formation of small droplets made easier. One has to visualize each one of these small droplets as surrounded with a more concentrated surface layer." Here the formation of the surrounding film and the reduction of the surface tension are attributed to the accumulation of soap particles at the interface of the two phases. This phenomenon is referred to as adsorption and it is from this idea that the adsorption theory for emulsions has been developed.

Bancroft[18] deduced the underlying principles of the modern theory. He accepted Donnan's surface tension, but pointed out some of its limitations, the chief of which was that Donnan only considered oil-in-water emulsions, two emulsion types were not considered. Bancroft considers the adsorption of particles at the interface an established fact. In his book he says[4]:

"If we call the two liquids "water" and "oil" and the emulsifying agent "soap" the emulsifying film has a minimum thickness of three molecules, one molecule of water, one molecule of soap, and one molecule of oil. There will be two surfaces to the emulsifying film, the one towards the water and the one towards the oil. If the surface tension of the water-soap interface is less than that of the oil-soap interface, the film will tend to curl so as to be convex on the water side and we shall have a tending to emulsify oil in water. If the surface tension at the water-soap interface is greater than that of the oil-soap interface, the film will tend to curve so as to become concave at the water side and we shall have a tendency to emulsify water in oil."

Adsorption, Positive and Negative. Adsorption in its widest meaning is the accumulation of particles at a surface. Adsorption at solid surfaces is restricted to outside region surrounding the solid surface. There is no such restriction with adsorption at liquid surfaces. Particles that are originally dissolved or dispersed in the liquid may migrate toward the surface from the inside and become adsorbed at the surface(56). Since most emulsions are prepared by dispersing the emulsifying agent in one of the phases before emulsification, this phenomenon of adsorption at liquid surface is of utmost significance in emulsions because the adsorptive force

will concentrate the particles at the interface. The process of particles accumulating at the liquid surface, causing a decrease in the surface tension, is called positive adsorption. The inverse process, that of thinning out at the surface and accumulating in the interior of the liquid, causing an increase in the surface tension is called negative adsorption[57]. Some of the organic compounds, such as soaps, certain proteins, and esters, are positively adsorbed and thus reduce the surface tension of the water. These are called surface-active agents, and emulsifying agents are a member of this group. Positive adsorption is the explanation given by the adsorption theory for the reduction of the interfacial tension and for the formation of the interfacial film.

The Gibbs Adsorption Equation. According to thermodynamics, processes which are accompanied by a decrease in free energy tend to occur spontaneously. Thus the fact that organic acids can lower the surface tension of water suggests that they will spontaneously be adsorbed on the surface so that the free energy of the surface will be decreased. The thermodynamics of surface adsorption was treated by Gibbs[26] in 1876. He derived an exact relationship between adsorption and surface tension.

$$\Gamma = \left[\frac{c}{-RT}\right]\left[\frac{d\gamma}{dc}\right] \qquad (1)$$

where, Γ = moles of solute per unit area of surface in excess of moles per unit area of body, (moles/cm^2).

c = concentration of solution, (gr-moles/cm^3).

R = gas constant, (ergs/°K mole)

T = absolute temperature, (°K)

$d\gamma/dc$ = rate of variation of Surface tension of solution with concentration, (dyne-cm^2/gr-mole).

If a solute causes a decrease in surface tension ($d\gamma/dc$ is negative), equation (1) shows that there will be adsorption of the surface. Therefore the surface will have a higher concentration of solute than the body of the solution.

If a solute causes an increase in surface tension ($d\gamma/dc$ is positive), its concentration in the surface region will be less than in the bulk of the solution.

Advantages and Disadvantages of Adsorption Theory. The merits of the adsorption theory are unquestionable; it is the basis of most of the modern speculation on the formation and properties of emulsions. On several important points, the adsorption theory goes far beyond any previous theory. It explains how the interfacial tension is reduced by the positive adsorption of particles of molecules at the interface. Second, it tells how the protecting film is formed by the adsorption of particles at the interface. Third, it shows why only a specific

type of substances, the emulsifying agent, is capable of producing permanent emulsions, because only these substances can be adsorbed at the interface. Fourth, it offers a possible explanation for the formation of either oil-in-water or water-in-oil emulsions. There are still several questions that are not answered by this theorem. No adequate explanation is given for the structure of the interfacial film and for the phenomena of breaking and phase reversal. Very little is revealed about the role of the emulsifying agents outside the fact that they are positively absorbed which gives no clue to their true nature.

Wedge Orientation Theory. The oriented wedge theory is essentially a theory for a special group of emulsifying agents - the soaps. This theory was presented by Finkle, Draper, and Hildebrand[13,19,27].

Cross-section of Molecules. This theory is based on the idea that the polar and nonpolar ends of a soap molecule have cross-sections of different sizes. It assumes that the molecules are not cylindrical but have the shape of small cones or wedges. An alkali soap is represented by the general formula:

$$RCOOM_I$$

where R stands for a long hydrocarbon chain and M_I for a monovalent cation, such as Na^+, K^+, or NH_4^+. The

polar groups $-COOM_I$ is assumed to have a larger cross-section than the non-polar hydrocarbon chain. The metallic soaps are represented by the following formulas:

$$\begin{matrix} RCOO \\ RCOO \end{matrix}\!\!>\!M_{II} \qquad\qquad \begin{matrix} RCOO \\ RCOO \\ RCOO \end{matrix}\!\!>\!M_{III}$$

Where M_{II} stands for a divalent cation such as Ca^{++}, Mg^{++}, or Zn^{++}, and M_{III} for a trivalent cation, for instance Al^{+++}. Therefore the non-polar end in the molecule of a metallic soaps is supposed to have a larger cross-section, because the di- or trivalent metals have two or three acid radicals attached to each metal atom. Thus, the soap molecules are described as little wedges which, because of their peculiar shape, force the interfacial film to curve.

Alkali Soaps. If an alkali soap molecule becomes adsorbed at the interface, the film will be bulkier at the water side, since the polar heads are bulkier than the non-polar tails. Therefore, the film will tend to curve concavely toward the oil and promote the formation of oil-in-water emulsion, as is illustrated in Figure 1.

Metallic Soaps. When a heavy metallic soap is added to a mixture of oil and water and the mixture is shaken, the molecules of the metallic soap, having a bulkier non-polar portion, will curve the film concavely toward the water as shown in Figure 2. This will cause the formation of a water-in-oil type of emulsion.

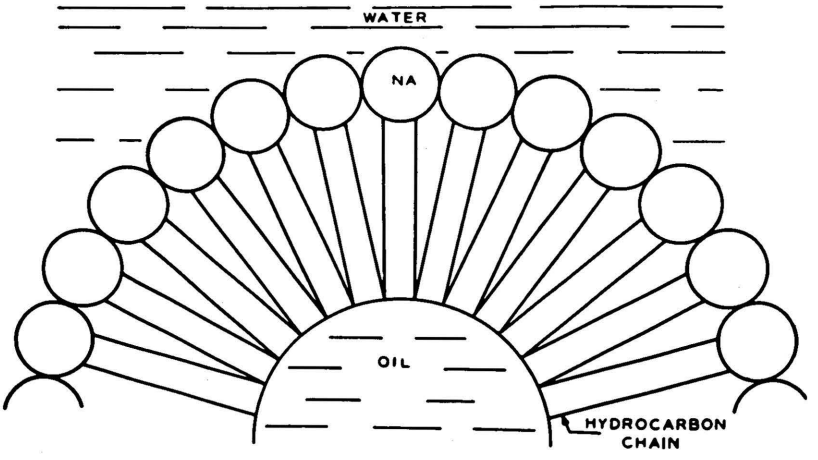


Figure 1. A Drop of Oil Held Emulsified in Water by an Alkali Soap According to the "Oriented Wedge" Theory.

Berkman, S., and G. Egloff: "Emulsions and Foams," p. 94. Reinhold Publishing Corp., New York, N. Y., 1941. 1 ed.

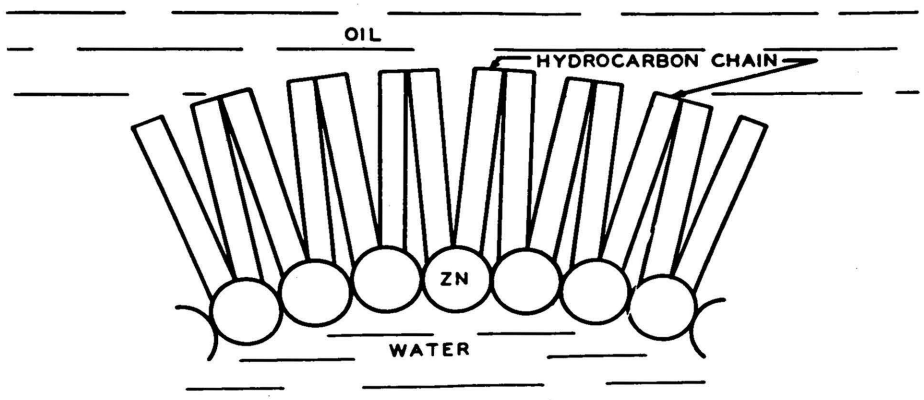


Figure 2. A Drop of Water Held Emulsified in Oil by a Heavy-metal Soap According to the "Oriented Wedge Theory"

Berkman, S., and G. Egloff: "Emulsions and Foams," p. 95. Reinhold Publishing Corp., New York, N. Y., 1941. 1 ed.

Advantages and Disadvantages of Orientation Wedge Theory. In this way, the oriented wedge theory accounts for the known fact that alkali soaps are oil-in-water emulsifiers, and metallic soaps promote the formation of water-in-oil emulsions. Although this theory is an interesting speculation, it is just another attempt to explain the type of emulsion formed on the basis of film curvature. There is very little experimental evidence for the wedge shape of the molecules. It is probably correct to assume that the polar end of sodium and potassium oleate is larger than the hydrocarbon chain tail; but the same must be true of the soaps of heavy monovalent metal, e.g., the silver salt of fatty acids which promote the formation of water-in-oil emulsions. Therefore the actual shape of the molecule appears to have less bearing upon the type of emulsion formed. The main objection to the oriented wedge theory is that it deals only with soap type of emulsifying agents and gives no explanation for the action of other type of emulsifying agents such as the cation active compounds and the nonionic type.

Bancroft[5] points out that the oriented-wedge theory is a special case of the adsorption theory. He says, "(Oriented-wedge theory) postulates that the colloidal emulsifying particles must have both polar and

non-polar groups upon their surfaces so as to be adsorbed at the interface. It is not clear how this will apply to carbon. With a bivalent base the fatty radicals which are in the oil tend to spread, making the water convex. This mechanical model does not account for the difference in behavior of a sodium and a silver soap. All that Hildebrand and Harkins really mean is that we get oil-in-water if the oriented molecule of the emulsifying agent is chiefly in the water phase, and water-in-oil if the oriented molecule is chiefly in the oil phase. If worded this way, the wedge hypothesis ceases to be an independent hypothesis and becomes a special case in the general (adsorption) theory."

It may be concluded that the different theories are not essentially antagonistic, but rather are different factors in a rather complex mechanism of emulsification.

Emulsifying Agents

The necessary conditions for forming a stable emulsion are that the droplets shall be so small (less than 1 micron) that they will stay suspended and that there shall be a sufficiently viscous or plastic film around each drop to keep the drops from coalescing. An emulsifying agent is therefore a substance which goes into the interface and produces a film having satisfactory physical properties.

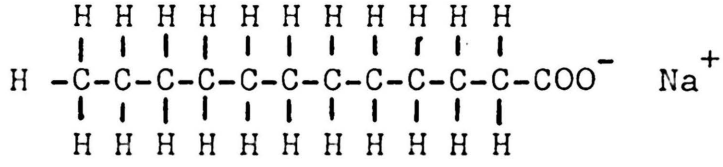
Requirements of Emulsifying Agents. There are five requirements that a substance should meet in order to be called an excellent emulsifying agent. They are: (1) It must reduce the interfacial tension, (2) It must stabilize the emulsion, (3) The agent must be chemically stable, (4) The agent should be selective. By selective, it is meant that the agent should promote very definitely one and only one type of emulsion; it should be distinctly hydrophilic or hydrophobic and not promote under certain circumstances oil-in-water emulsions and then under different conditions the opposite type. (5) The agent should be fairly odorless, light in color and cheap in use. The first three requirements are indispensable. Requirements number four and five are not essential conditions, but are advantageous[48].

Classification of Agents. Up to this point there has been no classification of the emulsifying agents other than the fact that some will form an oil-in-water emulsion and others will form a water-in-oil emulsion. This type of classification is appropriate for some instances, but for an understanding of why the emulsifying agents act as such, a chemical classification will give a better understanding.

A chemical classification of the different agents can be accomplished on a basis of the different ionization, or electrolytic dissociation. Many agents are electrolytes and act just as other salts, acids, and bases in dissociating in water.

The active part of the molecule that determines the properties of the agent may be in the anionic portion of the dissociated molecule, giving rise to the name anion-active agent. By the same reasoning, a dissociated molecule that has the active part of the agent in the cationic portion would be called a cation-active agent. Some agents do not dissociate at all, so they may be called non-ionic agents. A general classification of the agents according to the property of dissociation is given in Table II.

Anion-Active Agents. A good example of an anion-active agent is lauric acid soap.



(Lauric acid soap-ionized)

It can be seen that the anion is in the group $C_{11}H_{22}COO^-$; this is called the active group, as it contains the factors that are important in making the substance an emulsifying agent. The cation, in this case, is relatively unimportant. As can be seen from the listing of agents in Table II the anion-active agents comprise the largest group of agents used in the process of forming emulsions.

Amine soaps have proved to be one of the most useful of the anion-active type of agents[16]. Important properties of emulsions formed with amine soap are: (1) small particle size

TABLE II

Classification of Emulsifying Agents

Anion-Active Agents

Group 1. Soaps

a. Alkali Soaps

b. Metallic Soaps

Group 2. Organic Amino-Compounds Producing Soaps with Fatty Acids

Group 3. Sulfated Compounds

a. Sulfated Oils

b. Sulfated Alcohols

Group 4. Sulfonated Compounds

a. Aliphatic Sulfonates

b. Aromatic Sulfonates (also with Aliphatic Side-chains)

Cation-Active Agents

Group 5. Cation-Active Agents

Non-Ionic Agents

Group 6. Esters and Ethers

a. Hydrophobic

b. Hydrophilic

Miscellaneous Agents

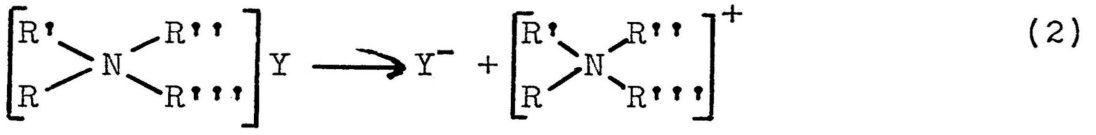
Group 7. Natural and Modified Natural Agents

Group 8. Dispersed Solids

Sutheim, G. M.: Theory of Emulsions and Emulsifying Agents, "Emulsion Technology," p. 326. Chemical Publishing Co., Inc., Brooklyn, N. Y., (1946). 2 ed.

(1 micron), (2) ease of preparation, (3) non-corrosiveness, (4) wide flexibility in making, (5) long storage stability, and (6) very slightly affected by temperature variations.

Cation-Active Agents. Cation-active agents may be represented with the general formula of a quaternary ammonium salt which dissociates in the following way[49]:



(2)

Here R represents a long hydrocarbon chain, whereas R', R'', and R''' represent shorter organic groups, such as methyl, ethyl, etc. Y stands for a salt-forming acidic group, such as Cl^-, Br^-, I^-, etc. The active group of this type agent is in the cation group, hence the name cation-active.

Complex organic compounds of this type agent containing a fatty acid chain in addition to an amino group are complete emulsifying agents in themselves. They may be formed by reacting long chain fatty acids with various ethylene amines. Cation-active agents show their greatest activity under acidic conditions. These emulsifiers are not affected by hard water and they retain their emulsifying characteristics even at exceedingly low concentrations.

Emulsions formed with cation-active agents have these characteristics: (1) controlled stability in presence of calcium or aluminum cations and in acid concentrations, (2) good lubricating characteristics, and (3) unusual ease in formulating and handling.

Non-ionic Agents. Agents of the non-ionic class may be represented by an ester of the general formula:

$$RCOOR'$$

where R represents long hydrocarbon chain, and R' represents a radical containing two, three, or a large number of alcoholic groups. Different agents of this class are hydrophilic, or oil-in-water agents, and others are hydrophobic, or water-in-oil agents.

Polyetheylene glycols of the general formula:

$$HOCH_2(CH_2OCH_2)_xCH_2OH$$

react with fatty acids to form mono- and di-ester derivatives. By the correct balancing of the molecular weights of the polyethylene glycols and the reacting fatty acids, emulsifying agents for many aqueous systems can be prepared.

Miscellaneous Agents. Natural and modified natural agents are a group of agents that are quite different chemically but very much alike physically. Generally, they are hydrophilic colloids, forming solution of high viscosity in water. Most of these agents are used as found in nature, or with only slight modifications, and usually are of the oil-in-water type. This large group has such members as[50]: (1) alginates, sodium or ammonium compounds of alginic acid, (2) carbohydrates, (3) water soluble cellulose derivatives, (4) water soluble gums, (5) lipids and sterols, and (6) proteins.

Solid particles, insoluble in both water and oil phase, can act as emulsifying agents, if they are in a state of very

fine dispersion. Examples of hydrophilic solid agents, forming oil-in-water emulsions, are clay, silica, and most silicates. Hydrophobic solid agents, forming water-in-oil emulsions, are represented by graphite, carbon black, and most aniline pigments.

For a powder or fine dispersion of solid particles to act as an emulsifying agent, the particles must be wetted to a certain extent by both liquids. If the interface is filled with the finely dispersed particles, its tendency to contract causes it to bend toward the least wetting liquid, making this least wetting liquid the dispersed phase[49]. If the particles are equally wetted by the two liquids, emulsification will not occur.

Methods of Producing Emulsions

In the process of emulsification, energy in some form must be supplied to tear the internal phase apart, to overcome the forces opposed to emulsification, and to keep the batch in motion until uniform distribution is obtained. Machines that can supplied this source of energy varied from the hand-worked mortar and pestle to power-driven apparatus. A selection of the type of equipments that can be used will be discussed, with the intention to illustrate general ideas rather than to give an exhaustive account of the different types.

Slow-running Mixture and Agitators. The first machines used for emulsification were probably simple mixers consisting

of a vat equipped with an agitator. This type of machine was not very effective. The blades of the agitator cut slowly through the batch and did not promote a uniform mixture. More than this is needed to produce a good emulsion; the internal phase has to be torn apart, and the shreds have to be stretched and disintegrated. Only for a certain medium consistency (particle sizes in the range between one and five microns) and only if the conditions of emulsification are thoroughly favorable, will a slow running machine produce a fairly good emulsion. Under adverse conditions, coarse emulsions of little stability will be obtained(8).

Colloid Mills. Colloid mills have come to be defined as - "machines whose functions are to disintegrate, disperse, emulsify and mix otherwise immiscible materials"(9). In this definition, nothing is said about the size of the dispersed droplets. Although the name "colloid mill" implies that the machine is capable of reducing the particle size of the dispersed phase to colloidal dimensions (between 0.1 micron and one micron), this is not always true, because the particle size of the dispersed phase in emulsions are usually far above the colloidal range. It is an established fact that the colloid mill improves the particle size of coarse emulsions considerably and yields products of improved stability and consistency(51).

Basic Principle of Colloid Mills. The general principle of the different types of colloid mills is the

same. The two essential sections are a rotor, the speed of which may vary from 1000 to 20,000 revolutions per minute, and a stator, the emulsion passing between the opposing faces of these two. The clearance between the stator and the rotor may be constant over the faces or they may vary in a number of ways, but means are usually provided for the adjustment of the clearance to any desired value, which can be checked with feeler gauges at certain points and may be as low as 0.001 inch. The mass is forced through the narrow clearance between the rotor and the stator. The shearing force which is developed in the narrow space between the revolving and the stationary portion achieve a thorough disintegration of coarse particles. Two forms of feed are available; the two phases of the emulsion may be fed into the machine simultaneously, or a previously mixed coarse emulsion may be treated to give a finer dispersion[31]. A following description will be given of some of the more common types of colloid mills.

The Manton-Gaulin Colloid Mill. Figure 3 shows a sectional view of the Manton-Gaulin colloid mill and Figure 4 shows the two-inch Gaulin Mill disassembled. In this mill, the material to be treated is introduced at A (see Figure 3) and is forced through the first stage gap B, by impellers located on the front rotor face. These impellers also act as cutters and shredders, breaking down thoroughly and disintegrating the material as

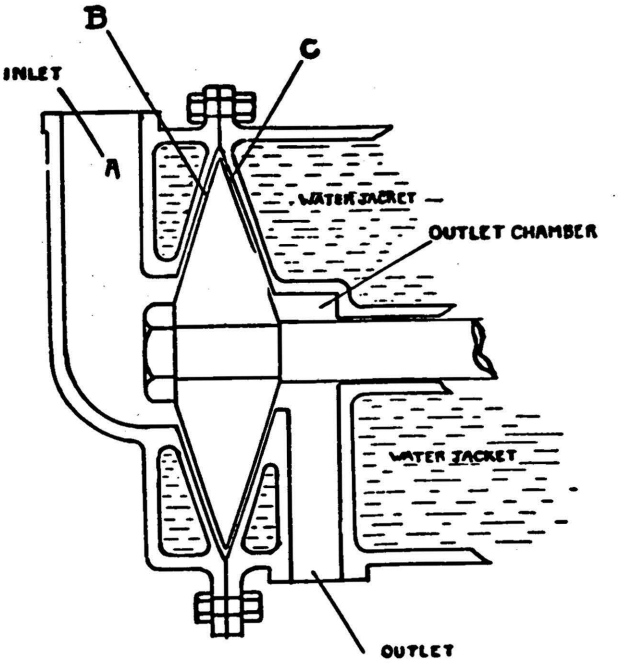


Figure 3. The Manton-Gaulin Colloid Mill

Sectional View.

Bennett, H.: "Practical Emulsions," p. 51. Chemical Publishing Co., Inc., Brooklyn, N. Y., 1943. 1 ed.

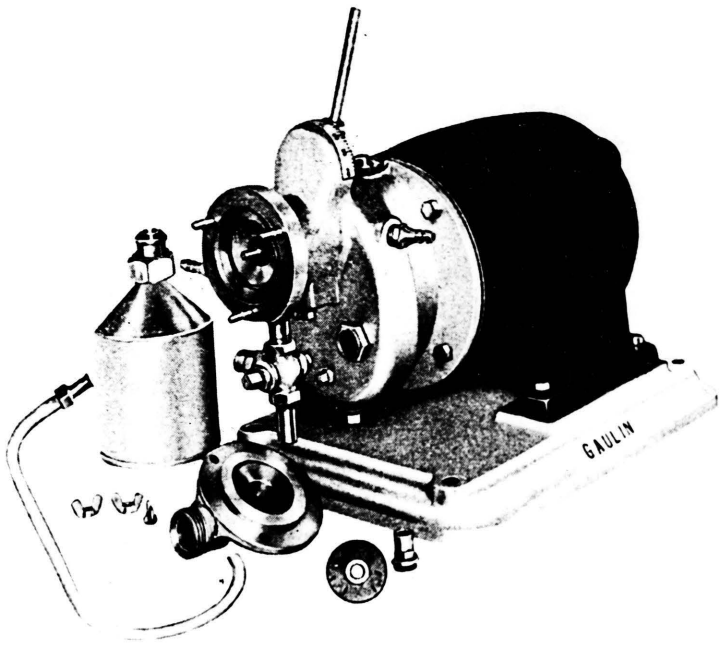


Figure 4. Gaulin 2" Mill Disassembled.

Bennett, H.: "Practical Emulsions," p. 51. Chemical Publishing Co., Inc., Brooklyn, N. Y., 1943. 1 ed.

it passes through. The pressure built up by the impellers forces the material across the outer edge of the rotor, then inward across the second stage or back face C, where it receives another finishing treatment. The product in its passage through gap "C" is traveling counter to the path of centrifugal force. This is of extreme importance. Material in the second stage enters the gap at the periphery, where it covers the maximum rotor area. From here the material is crowded and pushed into the diminishing gap area by pressure, and emerges at the center of the rotor, at practically no pressure. In its entire passage through the second, or finishing stage, the material receives the maximum possible rotor action. The second stage "C" can be adjusted while the mill is running by means of an adjusting dial which is calibrated in thousandths of an inch[10].

Premier Paste Mill. Figure 5 refers to a section of a 5-inch horizontal type mill which has working parts consisting chiefly of a rotor, a spindle RS, and a starter S, the working surface being at WS. The adjustment of distances between the stator and the rotor is made by slacking off the locking device LD and adjusting the clearance by means of the ring AR. The mill is driven by means of a very thin rubber belt on the pulley P. The normal speed of this mill is approximately 9,000 revolutions per minute. The material to be treated is fed

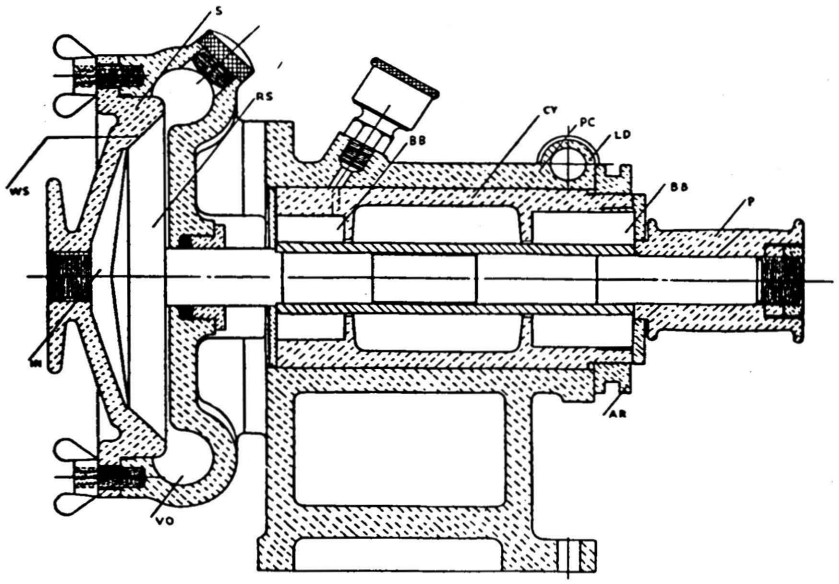


Figure 5. The Premier High Speed Colloid Mill.

Johnson, R. I.: The Design of Emulsifying Machines, "Technical Aspects of Emulsions," p. 35. A. Harvery, London, 1935. 1 ed.

in through the inlet IN, passes through to the working space WS and leaves by the volute VO[20].

A vertical type of mill, the so-called paste mill, has working parts similar in principle to the horizontal type mill. It is, however, directly driven from a vertical motor through a coupling. A jacket surrounds the stator to permit heating or cooling water to be circulated and the emulsifying faces of the rotor and stator are longer than those of the colloid mill[20].

Barlett-Snow Colloid Mill. This colloid mill with triple processing action is illustrated in Figure 6. The material is fed downward through a receiving funnel, A, and encounters the impeller vanes, B, on top of the rotor travelling at 10,800 revolutions per minute, which force it to the periphery of the rotor at pressures as high as 150 pounds per square inch for some materials. The material is sheared at C in passing downward between the side of the rotor and the housing, is then impelled against centrifugal force by the pressure of oncoming material through a labyrinth of tight-fitting circular rings, D, machined on the bottom of the rotor and the top of the stator, and then forced across the smooth section, E, between the rotor and the stator and drains from chamber F through the side discharge outlet[21].

Homogenizers. The designation "homogenizer" is usually employed for a type of equipment originally used in the milk

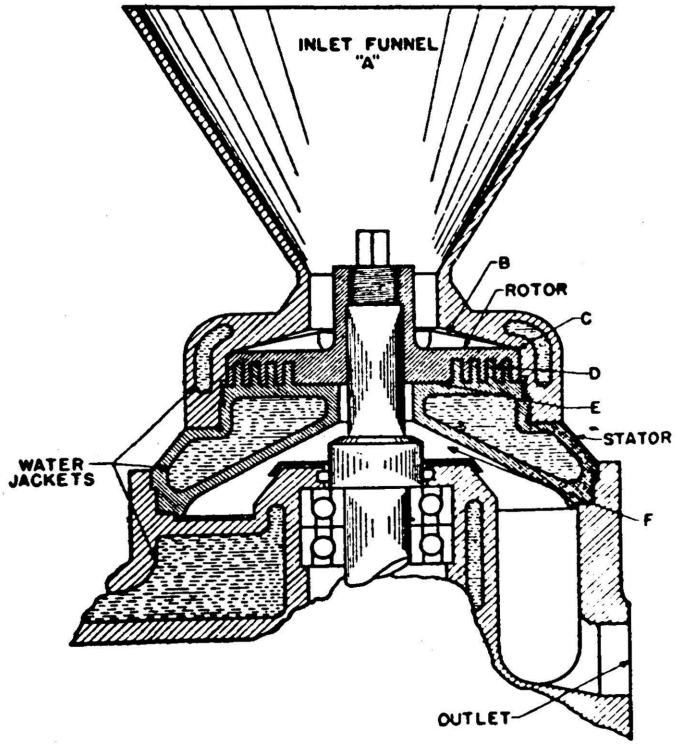


Figure 6. The Bartlett-Snow Colloid Mill.

Clayton, W.: "The Theory of Emulsions and Their Technical Treatment," p. 381. The Blakiston Company, Philadelphia, Penn., 1943. 4 ed.

industry to produce milk of small and uniform particle size (one micron) and improved stability. The process of homogenization consists essentially in passing the product under pressure between ground surfaces. High velocity, hydraulic shear, pressure release, and impact, rend the disperse phase into a very fine state of sub-division. The particles or droplets are reduced to one micron and less in diameter. In the homogenizing process, the reciprocating action of a plunger type pump forces the product between the valve seat and the valve. Pressure is applied by a handwheel which restricts the valve gap and the material is forced through by the pressure which is built up. Since the pressure is positive, receptacles on levels much higher than the homogenizer may be filled directly from the discharge pipe[11].

A great variety of homogenizers has been designed, all of which work on the principle of forcing the coarse mixture of the two liquids to be emulsified through a narrow orifice under high pressure as mentioned above. It would be very difficult to give an adequate description of the many different makes of homogenizers. Descriptions will only be given to illustrate the foregoing remarks and to give a general idea of the design of these machines with special reference to the homogenizing valve.

Brush Homogenizer. This homogenizing valve depends on the elasticity of a metal tube for its pressure loading which forms a system of very low inertia and tends

considerably to reduce the time lag of the valve in responding to pressure fluctuations. The valve, illustrated in Figure 7, consists of a tube, B2 of special metal, carrying and homogenizing face and a ring, B3, at each side of which homogenization is effected. The tube is fitted over a spindle BO, which extends its whole length and which is capable of lateral adjustment by means of a handwheel working through a differential thread. As the spindle is screwed into the chamber, pressure is increased. Another feature of this machine is a system of air-venting throughout the cylinder block which renders an accumulation of air at any point practically impossible[32].

Liquid is delivered from the discharge ports of the pump component of the homogenizer to the chamber in which the tube threaded over its rod, B2/BO, is located. The quantity, as a function of the pump speed, then raises pressure in the homogenizing chamber. This procedure, being directed through the cone entry of item, Bl, exerts a force on the homogenizing faces, stretching the tube B2 over its central rod, and so providing an aperture between the homogenizing faces at B3/Bl[23].

The Impulsor Emulsifier. The basic principle of this apparatus is the use of a pulsating action by which the liquid phases to be emulsified are subjected to alternate decreases and increases of pressure before

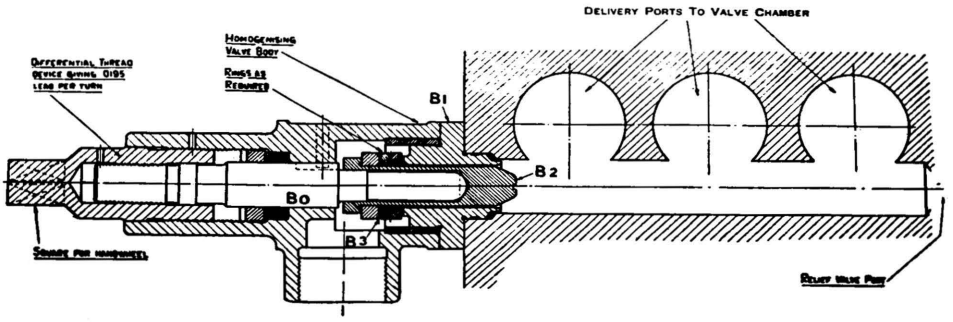


Figure 7. Sectional View of Brush Homogenizing Valve.

Clayton, W.: "The Theory of Emulsions and Their Technical Treatment," p. 400. The Blakiston Company, Philadelphia, Penn., 1945. 4 ed.

being ejected at a very high velocity through a narrow gap. The liquids are drawn into and intimately mixed in the cylinder by the suction action of a plunger. Disintegration is then effected by the shearing forces exerted during expulsion through the gap.

Figure 8 illustrates the Impulsor emulsifier. It consists of a cylinder, C, having two inlets, A, and an outlet head, D, within which a plunger, B, is made to reciprocate by means of a crank drive, G. The two phases of the emulsion can be fed in separately in desired volume ratio. At the suction stroke of the plunger B, some of the mixture is drawn into the cylinder through a non-return valve, which closes on the return stroke of the plunger. Pressure increases until it reaches a value predetermined by adjustment of the compression of the powerful outlet valve spring by means of the handwheel F. When this pressure is attained, the outlet valve C, opens and a portion of the mixture is ejected at high velocity between the valve face and its seating. The machine runs at 275 revolutions per minute and the liquids within the cylinder are subjected to cycles of compression and expansion at a corresponding rate, and in consequence undergo violent agitation[22].

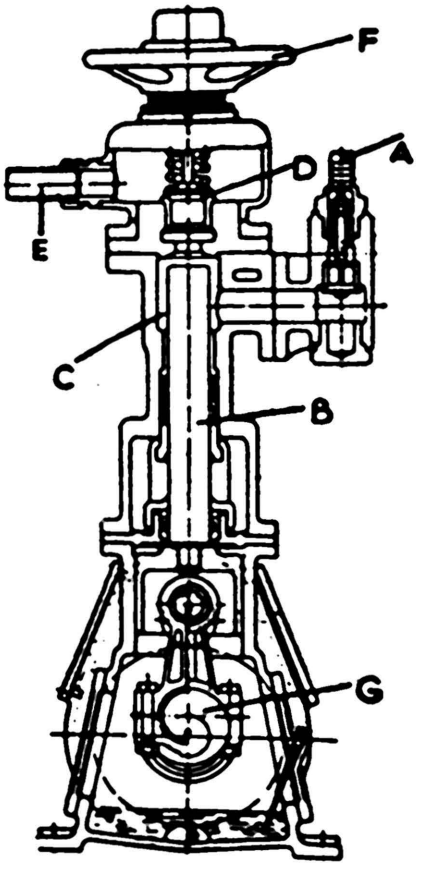


Figure 8. The Impulsor Emulsifier.

Johnson, R. I.: The Design of Emulsifying Machines, "Emulsion Technology," p. 116. Chemical Publishing Co., Inc., Brooklyn, N. Y., 1946. 2 ed.

Ultrasonic Energy. In 1927, Wood and Loomis[63] and Richard and Loomis[39] found that high frequency sound waves ("ultrasonics") of great intensity are able to produce a number of phenomena pertaining to the realm of colloid chemistry. They found that ultrasonics may bring about various dispersion effects, such as the mutual emulsification of two bulk liquid phases, the disintegration of certain solids, the depolymerization of high molecular substances, and the formation of fog. On the other hand, they also found that ultrasonics may cause accumulation, aggregation, coagulation, and many other physical and chemical effects. Of primary interest at this time is emulsification by ultrasonic waves. In order to do this subject more justice, it will be discussed under a new group heading of Ultrasonic Emulsification.

Ultrasonic Emulsification

The application of ultrasonics to the formation of emulsions is a relatively new and unique way of giving the necessary agitation to the two phases of the system. Before the mechanism of ultrasonic emulsification can be described, a brief discussion should be given on the nature and properties of ultrasonics, the different types of generators, and the role of cavitation.

Ultrasonic Waves. Above the frequency of audible sound, approximately 20,000 cycles per second, is the ultrasonic

range. Ultrasonic waves travel in straight lines, do not spread out, and are easily reflected by any change in density or elasticity of the material through which they are passing. In the past ultrasonics has been referred to as high frequency inaudible sound waves, but the term now probably includes intensity as well as frequency. The words ultrasonic and supersonic have been used synonymously, but current definitions use ultrasonic to refer to frequencies above audible sound waves, whereas supersonic refers to speeds of movement that exceed the speed of sound. The lower limit of the frequency of ultrasonics is approximately 18,000 to 20,000 cycles per second with a possible upper limit of 5×10^8 cycles per second[1]. Little work has been done in colloidal chemistry with frequencies above a million cycles per second owing to the excessive absorption of high frequency vibrations. A difficulty of low frequency, 20,000 cycles per second, is that amplitudes must be greater than those of high frequency waves, 1,000,000 cycles per second, to transmit a given quantity of energy[42]. At low and medium frequencies (20,000 to 200,000 cycles per second) the amplitude must be so large that the mechanical strength of vibrators limits the sound transmission, and unless amplitudes stay under the mechanical strength limit, a vibration crystal may be destroyed.

Ultrasonic Generators. It is beyond the scope of this investigation to discuss in detail the physical principles on which the construction of the different sound generating devices are based. Also, it is unnecessary to do so since these

are discussed in detail in a number of excellent references[24,28,59]. However, it seems imperative to discuss those types of sonic and ultrasonic generators which have been used successfully for colloid work. Four main groups of sound generators will be discussed.

Piezoelectric Transducers. Piezoelectric transducers transform high-frequency electric oscillations into mechanical oscillations by making use of the piezoelectric effect. Asymmetric crystals exhibit this piezoelectric effect. It will produce an electric charge when it is subjected to mechanical stress. If the sign of the stress is reversed, the polarity of the electric charges will be reversed. The converse effect was also found to be true, i.e., voltages applied to the faces of the crystal produced corresponding changes in dimensions. This change is due to mechanical stress produced by the electric force applied to the crystal. Some of the best known crystals that exhibit this piezoelectric effect are quartz, Rochelle salt, and tourmaline. Rochelle salt gives by far the greatest piezoelectric effect (roughly 75 times greater than quartz or tourmaline)[62], but on account of the inferiority of its mechanical properties its practical importance relative to quartz and tourmaline is greatly diminished.

Crystals of quartz possesses the piezoelectric property to a marked degree. Because they are strong

and hard, and do not appreciably deteriorate or corrode, they are utilized almost to the exclusion of all other materials for the electro-acoustic transducers needed for research on ultrasonics. Idealized crystals of quartz are represented in Figure 9. If an electric force is maintained in a direction X (see Figure 9), the crystal becomes strained in that direction. A quartz transducer for production of ultrasonic energy is made by cutting from the crystal a square plate or a disc with its thickness parallel to a direction X. The parallel surfaces of the plate are coated with metal (called electrodes) and when a potential difference is applied to them, the thickness of the plate will change. If the applied voltage alternates the plate vibrates in the direction of its thickness. In general these vibrations are forced vibrations and are extremely small, but if the frequency of the applied voltage be varied until it coincides with the natural frequency of the thickness vibration of the plate, resonance occurs and the amplitude of vibration is increased hundreds of times[60].

Vacuum tube high frequency generators are invariably used to provide the electrical oscillations necessary to excite the quartz plate. Figure 10 gives the elements of a circuit which can be employed for this

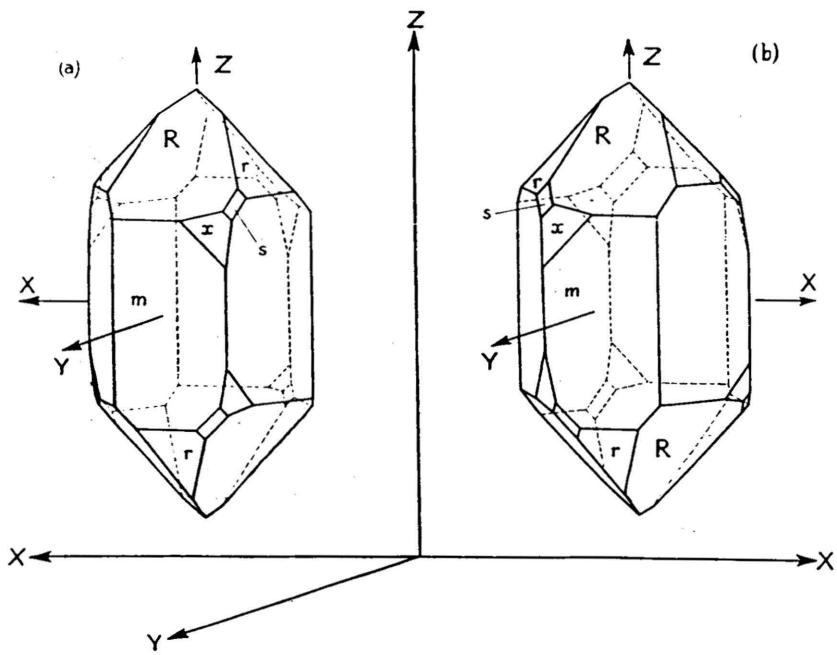


Figure 9. Idealized Quartz Crystals with Axes Indicated.
(a) Right-handed Crystal. (b) Left-handed Crystal.

Vigoureux, P.: "Ultrasonics," p. 8. John Wiley and Sons, Inc., New York, N. Y., (1951). 1 ed.

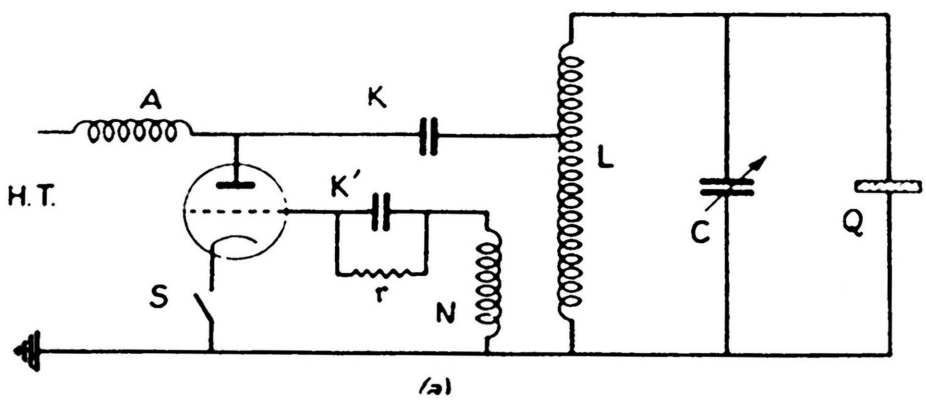


Figure 10. Circuit Diagram of High Frequency Vacuum Tube Generator Driving Quartz Transducer.

Vigoureux, P.: "Ultrasonics," p. 16. John Wiley and Sons, Inc., New York, N. Y., (1951). 1 ed.

purpose. The vacuum tube oscillation in Figure 10 can readily be adapted to high power or low power; all that is necessary is to change the high-tension voltage line.

The Magnetostriction Generator. The magnetostrictor transforms alternating electric currents into sound vibrations, making use of the magnetostriction effect. If a rod or tube of ferromagnetic material, perferably nickel, is brought into a magnetic field parallel to its axis, it decreases or increases in length, depending upon the material, its previous treatment, and the applied field strength. This effect is known as "magnetostriction"[41].

In an alternating magnetic field the length of the ferromagnetic vibrator changes periodically by magnetization, the alternating magnetic field being produced by an alternating electric current. Resonance between the natural elastic period of the magnetostrictive oscillator and frequency of the magnetic field increases the amplitude of the mechanical vibrations and also increases the efficiency of the transformation of electrical into mechanical energy[42].

The range of the useful application of the magnetostriction sound generators is from a few thousand up to 50,000 cycles per second. The corresponding relatively great sound wave length is in many cases a disadvantage for work in liquid systems. The advantages

of the magnetostriction sound generators are their relatively simple and cheap construction and the fact that the oscillator itself may, in most cases, be brought in direct contact with the substances to be treated. Magnetostriction sound generators are more economical to construct than piezoelectric equipment and can be built readily in large sizes, and multiple units seem entirely feasible.

The Electromagnetic Sound Generators. The frequency of this type of generator is entirely in the audible range. So far, these generators have been used in only a few cases in liquid systems. There are two types of oscillators; one of conventional electromagnetic design, and one of the Fessenden type. The electromagnetic oscillators are similar to those used in submarine communication and echo depth sounding; they consist essentially of a heavy steel membrane actuated by an electromagnetic field of resonance frequency. The oscillators of the Fessenden type have the vibrating membrane fixed to a copper tube. The movement of the diaphragm depends on the reversal of eddy currents of resonance frequency in the copper tube, induced by current oscillations in activating coil[1].

At the present time, it is difficult to fully appraise the merits of the electromagnetic sound generators

for use in liquid systems, since only a few investigators have used them.

Jet Edge Sound Generator. The jet-edge generator is a fluid dynamic device, involving vortex formation, in which stabilization is achieved by hydrodynamic feedback between a jet and an edge. Transducers of this type appear to be very promising for liquid phase processing. The resonant features required for high stability and output at cavitation levels can be obtained in a liquid jet system by a rectangular plate which vibrates in flexure. Two types of mounting of such a plate are possible: cantilever clamping and half-wave nodal support. In the first case a rigid and massive clamping block is required, and for the half-wave nodal support, the mounting is provided by two pairs of stiff and short pins which are held in position a distance of half-wave length apart. In both types of mounting the sharp front edge of the plate is aligned with the jet nozzle so as to split the stream. Figure 11 shows the arrangement for a half-wave supported flexural plate which offers the lease amount of obstruction to the liquid flow. The dimensions indicated in this figure must meet the following conditions: wedge angle $\alpha \simeq 30°$; nodal spacing $f/2 = 0.49L$; $d \leq t$, and $L \geq 2W$, where: L is the length of the nodal plate, t is the thickness of the nodal plate, W is the width of the nodal plate, and d is the width of the jet nozzle[29].

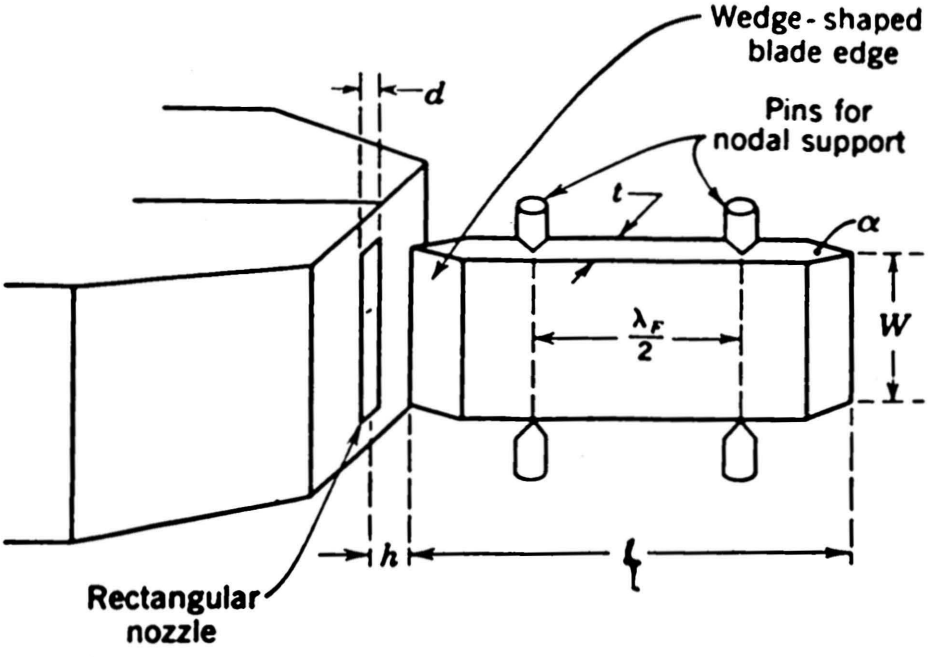


Figure 11. Jet-edge Generator for Liquids.

Hueter, T. F., and R. H. Bolt: "Sonics," p. 291. John Wiley and Sons, Inc., New York, N. Y., (1955). 1 ed.

In this type of a system, some sound is radiated from the vibrating plate, but the zone of greatest intensity is located on either side of the wedge-shaped front edge of the plate. Here the cavitation may be so strong that even plates made of hardened steel are damaged by cavitation erosion. The most promising application of such liquid jet transducer is in emulsification. They are superior to the electronically operated magnetostrictive and piezoelectric systems with respect to cost, maintenance, and ruggedness[30]. Emulsification of two liquid components can be achieved in two ways: (1) by immersion of the transducer into a tank filled with the one component and injection of the other component through the jet; or (2) by simultaneous injection of both components after some amount of premixing.

A commercial device for liquid-flow processing is illustrated in Figure 12. The distance between plate and nozzle can be adjusted by turning the knob at the extreme right. If plates of different size are used, the frequency can be adjusted in the range between 1 and 5 kilocycles per second.

Cavitation. The phenomenon of cavitation refers to the formation and violent collapse of small bubbles or cavities in the liquid, as a result of pressure changes[2]. When

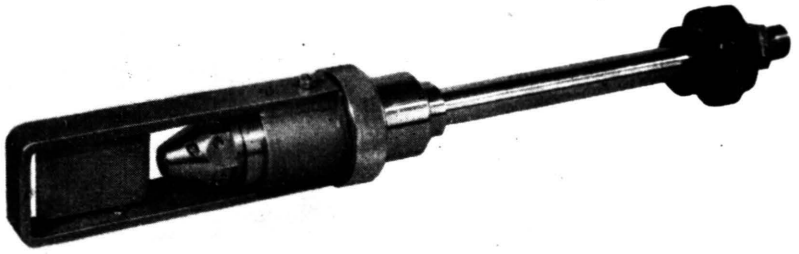


Figure 12. Commerical Jet Transducer.

Hueter, T. F., and R. H. Bolt: "Sonics," p. 293. John Wiley and Sons, Inc., New York, N. Y., (1955). 1 ed.

the pressure increases, the cavities collapse with a violent hammering action which generates local pressures up to thousands of atmospheres and local temperature up to a few hundred degrees.

Cavities, gas or vapor filled, ranging in size from submicroscopic to large enough to be seen by the naked eye, may be formed in a liquid by chemical, mechanical, or thermal action. Cavitation can occur in a liquid system when the total pressure at a point in the liquid is reduced to the vapor pressure of the liquid, and may be produced in a liquid by the application of high intensity ultrasonic waves. A liquid undergoing ultrasonic treatment is subjected to cyclic compression and tension; rupture of a liquid by this manner depends greatly on the magnitude of the tension, or negative pressure, during the rarefaction phase of the ultrasonic wave in the liquid.

Conditions Favoring Cavitation. Cavitation will not occur in every liquid system insonated by ultrasonic waves. Cavitation depends on intensity of the wave, physical condition of the liquid, and surrounding conditions. Samsel[40] found that the general intensity level required for cavitation in a liquid system under one atmosphere pressure is approximately 0.3 watts per square centimeter. Factors which affect cavitation include the viscosity of the medium, the amount of gas dissolved, the number of nuclei present within the

medium, the nature of these nuclei, and the vapor pressure of the medium. The presence of dissolved gases or nuclei in the liquid system is a necessity in order for cavitation to take place[61]. Dissolved gases create weak spots in stretched liquid and thus promote cavitation. An ambient pressure of approximately two atmospheres has been found to be the most favorable condition for cavitation[15].

Pressure Developed From Collapse of Cavity. It was mentioned above, that cavities collapse with a violent hammering action which generates local pressures up to thousands of atmosphere. Most of the chemical effects of cavitation are due to this violent collapse of the cavity which include emulsification by ultrasonic energy.

Lord Rayleigh calculated the pressure developed during the collapse of a spherical cavity. The result of his derivation is given by the equation[37]:

$$\frac{P'^2}{2\beta'} = \frac{1}{2}\rho U^2 = \frac{P}{3}\left[\frac{R_o^3}{R} - 1\right] \qquad (3)$$

where:

P = the pressure at infinity external atmospheric pressure

R_o = the initial radius of the cavity

β = the coefficient of compressibility

P' = the correlated pressure of the cavity during the collapse

R = the correlated radius of the cavity during the collapse

U = the velocity of the liquid

ρ = the density of the liquid

Using the preceding equation, Lord Rayleigh found that the pressure developed by the collapse of a cavity in water to be 10,300 atmospheres or 68 tons per square inch[37].

Rayleigh's calculation shows that pressures of thousands of atmosphere may be developed at the moment when the cavity collapse to a small fraction of its original diameter. Such collapse can cause the release of an enormous amount of energy which may be utilized.

Mechanism of Ultrasonic Emulsification of Two Immiscible Liquids. Since the work of Wood and Loomis[63], it has been known that high intensity sound waves readily bring about the formation of emulsions in two liquids system. The mechanism of this phenomenon has been investigated more than once, but no satisfactory explanation was given until Bondy and Sollner[14] published their paper in 1935. They found that cavitation was an important factor in the emulsification of two immiscible liquids by ultrasonic waves. Sollner[43] states that cavities, which are formed in the liquid, collapse with a violent hammering action which causes local pressures up to thousands of atmosphere. This destructive and disrupture violence has a high shearing force which will break up the oil into droplets and disperse them into the other liquid.

Effect of Pressure on Ultrasonic Emulsification.

The effect of external pressure on the formation of emulsions was demonstrated by Bondy and Sollner with an air saturated system of toluene and water, using no stabiliz-

ing agent. The absolute pressure over the sample being insonated was varied from a low vacuum to approximately five atmospheres, or 4000 millimeters mercury. Below a pressure of 100 millimeters mercury, it was found that no emulsification took place. Highest percentage of the dispersed phase, 5.7 per cent, was obtained at 1500 millimeters mercury pressure, approximately two atmospheres. On increasing the pressure above 1500 millimeters mercury it was found that the percentage of dispersed phase decreased again, going down to 1.2 per cent at a pressure of 4000 millimeters mercury. Pressures below 100 millimeters mercury were not sufficient to cause collapse of the formed cavities, and the resulting emulsifying action. Emulsification cannot take place when the liquids are in a vacuum or under a high pressure. This fact is evidenced by Figure 13 which shows two test tubes, each containing two immiscible liquids. One test tube (marked vacuum) has its vapor space evacuated and no emulsification would take place; the other test tube contains a gas vapor space under a slight pressure and emulsification is being accomplished by ultrasonic waves. Cavities may be formed by ultrasonic waves in a vacuum, but lack of outside pressure prevents their violent collapse. No emulsification takes place under high hydrostatic pressure because the pressure prevents the formation of cavities.

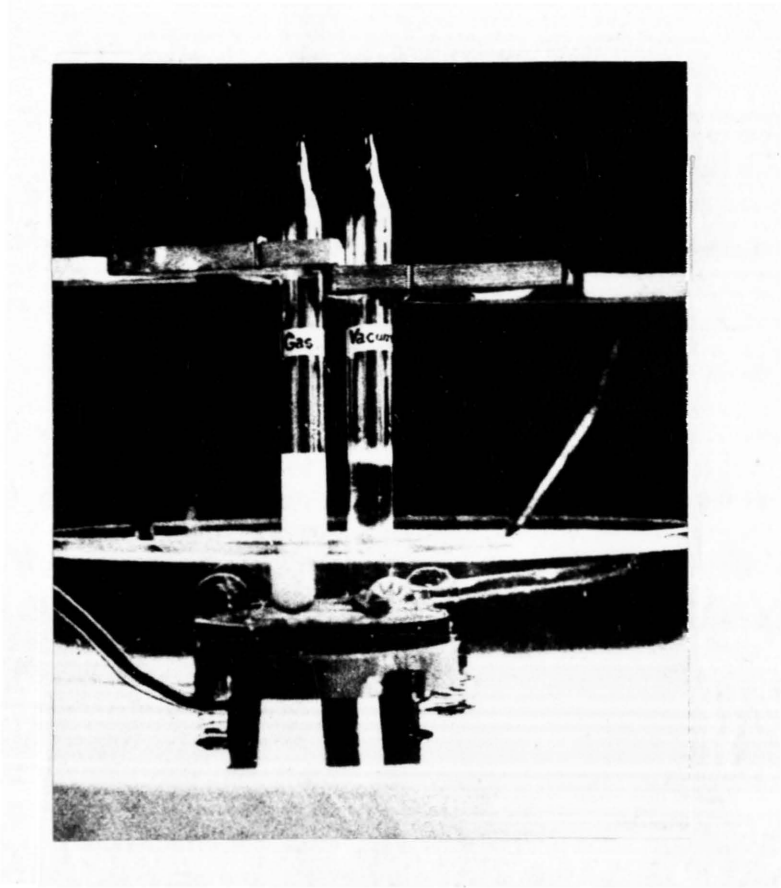


Figure 13. The Influence of Gas Pressure upon Emulsification.

Sollner, K.: Colloidal Effects of Ultrasonics, "Ultrasonic --two Symposia". Chem. Eng. Sym. Series No. 1, 47, p. 29 (1951)

Ultrasonic Intensity Required for Emulsification. It has been reported that an intensity of approximately 10 watts per square centimeter is required for good emulsification[42]. Cavitation in water has been reported to occur at an intensity of 0.3 watt per square centimeter[35,38]. Since emulsification of two liquids depends on cavitation, the effect of such variables as liquid viscosities, different liquid densities, hydrostatic pressures, and interfacial tension, can be seen by comparing the figures just given. The value of 0.3 watt per square centimeter is a minimum value required for cavitation in water under atmospheric conditions. The value of 10 watts per square centimeter indicates that much more than a minimum value of energy must be applied to produce good emulsification in a two phase liquid system, taking into consideration the additional energy required to overcome the cavitation suppression caused by the discussed variables.

The Effect of Temperature upon Emulsification with Ultrasonic Waves. Ultrasonic waves have a very pronounced heating effect upon liquids[63]. In emulsification with ultrasonic waves, heating takes place at the oil/water interface; a greater temperature rise with increased dispersion of the oil resulting from the increased interface. Frictional forces between the liquid and the transversely vibrating walls of the container causes the liquid to heat up.

To determine the effect of temperature upon emulsification with ultrasonic waves, Beal and Skauen[7] made a series of emulsions with and without cooling of the oil bath in the piezoelectric transducer assembly. Because it is impossible to achieve isothermal conditions in ultrasonic treatment of liquids, the temperature control of the cooling bath was not complete. However, they were able to control the temperature so that a rise of not more than 20 °C was achieved. They found that cooling the emulsions during exposure to ultrasonic waves did not increase the dispersion of the oil, as had been suggested in the literature. It is to be noted that in investigation by previous authors, they were concerned with emulsification without emulsifying agents; in the investigation by Beal and Skauen, a protected emulsion was considered. It was also found that those emulsions which were cooled during formation were consistently less evenly grained and showed globules with equal or larger "root mean cube diameter" than emulsions made without cooling.

Effect of Time of Exposure upon Emulsification With Ultrasonic Waves. Beal and Skauen[7] made a series of emulsions with exposure time of three, five, seven and a half, ten, fifteen, twenty, and thirty minutes. They reported a decrease in the "root mean cube diameter" of the globules with an increase in exposure times as in-

dicated in Figure 14. This is contrary to the results of Bondy and Sollner[15] who reported that after emulsification is complete continued exposure to ultrasonic waves leads to an increase in particle size in spite of the presence of an emulsifying agent. It is possible that longer exposure times by Beal and Skauen could lead to an increase in globule size, but up to thirty minutes this was not evidenced.

Effect of Orientation of Exposure Chamber above the Crystal Upon Emulsification. The importance of orientation of exposure chamber above the vibrating crystal was indicated by Richards and Loomis[39]. By lowering a beaker of water by means of a micrometer screw and exposing it to ultrasonic vibrations at several points in its descent they found a maximum temperature rise at points where an exact number of half-wave lengths separated the bottom of the beaker and the quartz crystal. The greatest amount of energy entered the beaker where the bottom of the beaker was in resonance with the waves traveling from the surface of the crystal. Beal and Skauen[6] studied effect of orientation of the exposure chamber above the crystal upon emulsification. They found that when the bottom of the exposure chamber was at points approximately a half-wave-length apart in the lowering of the exposure

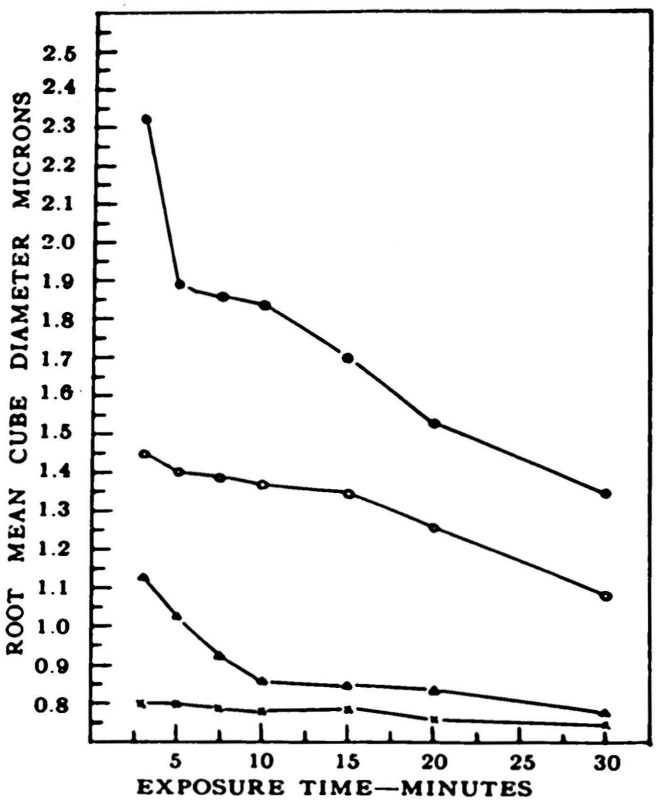


Figure 14. Effect of Time of Exposure to Ultrasonic Waves upon Emulsification with Hard Soap U.S.P.

Beal, H. M., and D. M. Skauen: A Study of Emulsification with Ultrasonic Waves II, J. Am. Pharm. Assoc. 44, 492 (1955).

chamber toward the crystal there was a rise in particle count and a decrease in "root mean cube diameter".

Characteristics of Emulsions formed by Ultrasonics. No outstanding characteristics, wanted or unwanted, have been found for emulsions prepared by ultrasonic waves over those formed by the conventional method. The concentrations and particle size vary greatly according to the material used, the intensity of the irradiation, and the size and shape of the reaction vessel. However, emulsions formed by ultrasonic insonation appear to have somewhat smaller particle size and slightly better stability than those formed by mechanical means.

So far no definite cost studies have been made in the application of ultrasonics to emulsions. No statement can be made in regard to the economic relations between ultrasonic emulsification and conventional agitations methods as to which one is the best until some means of accurately determining the power put into a liquid system by ultrasonic waves is found. However, in the pharmaceutical industry, it is believed that ultrasonic emulsification may be economically applicable for handling high-cost, low-volume liquids.

Effect of Ultrasonic Waves on Emulsifying Agent. Intense ultrasonic waves are known to bring about chemical changes in compounds which come into contact with them[34]. In solutions of the type represented by the gums, soaps, etc., there exists a type of structural arrangement posses-

sing properties similar to those of an elastic solid. Such fluids are said to possess structural or anomalous viscosity. Freundlich and Gillings[25] have shown that ultrasonic waves destroy this structure and thereby reduce the viscosity of the solutions. Beal and Skauen[6] treated solutions of emulsifying agents with ultrasonic waves for periods of seven and a half, fifteen, and thirty minutes. They found that solutions of polyethylene glycol 400 monostearate, tragacanth, and hard soap solutions showed significant losses in viscosity while those of acacia, sodium lauryl sulfate, and polysorbate 80 showed no significant change. In pharmaceutical emulsions the emulsifying agent contribute to the stability in part due to the viscosity of their solutions. This lowering of viscosity would be undesirable in pharmaceutical emulsions. In emulsification with ultrasonic energy this would necessarily be a consideration in the selection of an emulsifying agent.

Stability of Emulsion

There is one outstanding property of emulsions that is sometimes called the nightmare of the emulsion chemist. It is the stability of emulsion. The most perplexing problems in emulsification are probably found in the studies of stability. What is meant by stability of emulsion? Why is it a perplexing problem? No proper definition or theory has

been given to define or explain what is meant by emulsion stability. King and Mukherjee[33] made the following statement concerning stability: "...the most fundamental quality of emulsion stability is undefined, misunderstood and, at the best, regarded as a vague, empirical concept, while at the same time being of the utmost practical importance." Sutheim[52] made the following statements concerning stability: "It is my belief that there is no such thing as a stability which is typical of all emulsions, but only conditional stability with regard to the purpose of the emulsion. Therefore, it may be sufficient, although not very scientific, to describe emulsion stability as follows: We call an emulsion practically stable when it remains without major changes for a period of time long enough to fulfill the purpose for which it is designed."

Perhaps the best way to understand the problem of stability in emulsions is to discuss the various things that causes instability to occur in emulsions.

Creaming of Emulsions. Creaming is a term borrowed from the well known phenomenon in milk. Creaming is a rather uniform accumulation of emulsified particles. This accumulation of the dispersed phase may rise to the top or settle to the bottom, depending on the specific gravity of the internal phase with respect to the external phase. Therefore creaming can be considered to be a special case of sedimentation. This cream layer can be described as a more

concentrated emulsion, or to be more technical, as an emulsion with a higher ratio of internal phase. Creaming should not be confused with the breaking of emulsion. Breaking is the irreversible disruption of the emulsion, whereas creaming is a reversible stratifying of the dispersed droplets in a perfect state of emulsification. Gentle stirring or shaking will, in most cases, restore the original distribution of the emulsion. Although creaming is not one of the major factors which causes instability in emulsions, it is important in the study of stability.

Phase Reversal. Phase reversal is the phenomenon of the internal phase becoming the external phase, and visa versa. Phase reversed is considered to be a major instability even though the reversal emulsion is still an emulsion and may be more stable than the original type. But reversal renders the emulsion useless for the purpose for which it was designed. Phase reversal may be brought about by chemical action, by changes in temperature, or by mechanical means.

The Emulsifying Agent and Stability. Any change the emulsifying agent may under go, once the emulsion is formed, will derange a well established equilibrium in the system and endanger the stability of the emulsion. Unfortunately, an ideal emulsifier does not exist that will not be influenced by chemical or physical changes. Normally, the agents are likely to be affected by the constituents of either phase, particularly by the water phase.

Hydrolytic Decomposition of Emulsifying Agent. Emulsifying agents are attached to a varying degree by water. For soaps, the hydrolytic decomposition proceeds according to the general formula:

$$RCOONa + H_2O \rightleftarrows RCOOH + NaOH \qquad (4)$$

or for agents of the ester type:

$$RCOOR' + H_2O \rightleftarrows RCOOH + HOR \qquad (5)$$

Under normal conditions most of our emulsifying agents are little affected by hydrolysis. However, in emulsions conditions are not normal. The agent at the interface is spread over a huge area and offers an enormous surface to any attack. A reaction which is comparatively slow under normal conditions, may become vigorous in this state of fine dispersion. We also have to consider that hydrolysis at the interface, with oil at the one side and water at the other, proceeds under quite unusual conditions. To make things still worse for the emulsifier, the water phase is frequently loaded with ingredients which definitely increase the capacity of pure water to hydrolyze; namely, acids, alkalies, salts, or, in brief, various electrolytes.

There several ways to avoid emulsion failure due to hydrolyzation of the emulsifying agent. The easiest solution, of course, would be to avoid the use of agents of low resistance. Soaps and proteins are rather poor in this respect, sulfated and sulfonated agents are

much better, and the non-ionic agents are probably the best. Unfortunately, the agents of good resistance are more expensive and we have the problem of which is the most economical. Since it is the water phase that causes all the troubles of hydrolytic decomposition, the addition of a hydrophilic colloid will inactivate the water to some extent. It does this by binding the water firmly and producing what is called the hydrated complex. In this state, the water is neither free, nor chemically bound, but in some intermediary states, it is, so to say, handcuffed and less aggressive[53].

Bacterial Decomposition of Emulsifying Agent. Another cause of serious trouble is the action of micro-organisms upon deteriorable agents. Micro-organisms are almost omnipresent. Whenever they find something to eat that suits their taste, they start to feed and to reproduce at an amazing rate. Within a short time, millions of them are nibbling away upon the material that is supposed to protect the emulsion. Fortunately, not all the ingredients used in the emulsion find the approval of these little gluttons. Some substances are altogether unpalatable for them, while other substances they like immensely. The use of such substances involves real danger for the emulsion. Proteins are probably the most sensitive, carbohydrates and the mucilages, like gum

tragacanth, are also easily attacked, and all fat-containing substances can decompose under the influence of bacteria.

The simplest solution for troubles from this source would be not to use sensitive agents in the formulations. But these types of agents offer advantages with regard to price or performance, which does not permit us to cut them out altogether. When these types of agents have to be used, sanitary measures should be taken and the addition of preservatives is indispensable. This is necessary in order to protect the emulsion after it is manufactured, during storage, and until it is finally used up.

The Phase-Volume Ratio and Stability. The phase-volume ratio is the ratio of the volume occupied by the internal phase to that of the external phase. An emulsion with a high phase-volume ratio is called a concentrated emulsion, and one with a low ratio is called a dilute emulsion.

As in other fields, the ratio between constituents has something to do with the system's stability. In emulsions, the amount of internal phase you can force into the system has its limits, but there is no sharp "saturation" point. Rather concentrated emulsions and also rather dilute emulsions of good permanence can be made, but there is a zone of maximum stability, and the more you depart from that zone, the less favorable the stability conditions will become.

Although there are emulsions with as much as 99 per cent internal phase[36], practice actually shows that if the volume of the internal phase is increased above 74 per cent, the stability will decrease. On the other hand, very dilute emulsions are not very stable. The safest zone for forming stable emulsions is in the neighborhood of a phase-volume ratio of 50:50, and any excessive deviation from this optimum ratio will decrease the stability.

Viscosity and Stability. The viscosity of an emulsion is dictated by three main factors: the viscosity of the external phase, the phase-volume ratio, and the particle size. It is rather independent of the viscosity of the internal phase, because the dispersed droplets are thoroughly isolated by a protective film. The viscosity of the external phase is one of the decisive factors and one that can easily be controlled in the formulation of the emulsion. High viscosity of the external phase is definitely favorable for the stability of the emulsion. A highly viscous external phase decreases the speed of creaming, prevents, or at least retards the breaking of the emulsions, as well as the reversal of the phases. For both types of emulsions there are a number of swelling and bodying agents which will impart high viscosity at low concentration. For oil-in-water emulsions the bodying agents are the hydrophilic colloids, like proteins, and water-soluble cellulose ethers. For water-in-oil emulsions, metallic soaps, such as aluminum sterate or calcium linoleate, are much in use.

The phase-volume ratio is another factor of considerable influence upon the emulsion viscosity. Dilute emulsions have nearly the same viscosity as the pure external phase. Its few dispersed droplets, floating freely in the surrounding liquid, contribute little to the internal friction of the system. If the ratio of the internal phase is increased, the viscosity will also rise. At a certain point, usually when the phase-volume ratio is somewhere near the critical 74 per cent, the emulsion will become very viscous.

The particle size of the dispersed droplets has less influence upon the viscosity of the emulsion than the two factors previously discussed. However, experience shows that a fine emulsion is more viscous than a more coarse one, e.g., in homogenized milk, homogenizing the milk definitely increases the viscosity.

Particle Size and Stability. The stability conditions in emulsions are best if the particles are small (approximately one micron) and uniform in size. Emulsions with large particles (greater than five microns) have a strong tendency to cream and extremely large particles, above 25 microns, may either indicate insufficient emulsification or a beginning decomposition of the emulsion. The optimum range of particle size in emulsions is obtained by proper formulation, and by the use of efficient emulsifying equipment.

Temperature and its Effect on Stability. It is an undeniable fact that emulsion are temperature sensitive.

Numerous emulsions will break if exposed to low temperatures; others will break if exposed to high temperatures. As a rule emulsions are formulated to possess optimum stability at room temperature, between 40 °F and 80 °F.

The Influence of Heat. Elevated temperature may cause changes in the emulsion stability in several ways. (1) Heat will decrease the viscosity. As stated previously, this is an undesirable property. (2) Heat transforms some of the emulsifying agents from effective colloidal solutions into ineffective molecular solutions. Soaps, and many other hydrophilic agents produce heavy colloidal solutions by binding water and forming hydrated complexes. At elevated temperature, these complexes are broken up and the individual molecules become thoroughly water soluble. (3) Heat increases the speed of most reactions considerably. This is likely to cause the emulsifier to decompose and increase the possibility of hydrolysis. (4) Heat may cause volatile ingredients to evaporate. Emulsions, stabilized by soaps with a volatile alkaline component, such as ammonia or morpholine, may suffer.

It should be pointed out that heat will improve the stability of emulsions. As the temperature rises, it will decrease the surface tension and interfacial tension. It also speeds up the Brownian movement. On the

whole, it may be better to keep the emulsions below the boiling point of water, since the detrimental factors of heat have a stronger influence than those that are helpful.

The Influence of Cold. As a rule, cold affects emulsions only if the temperature goes below the freezing point of water. If the water phase actually freezes, trouble can be expected for the following reasons: (1) The water expands on freezing. This may cause considerable pressure to be developed and may lead to the crushing of the interfacial film. (2) Water usually freezes with the formation of sharp edged crystals which may also rupture the protecting film. (3) Many emulsifying agents form hydrated complexes. When the water phase freezes, a peculiar process sets in, freezing out. The aqueous solution does not freeze homogeneously but more or less pure water freezes out and, thus it is withdrawn from the hydrated complex. This process is usually irreversible, and on thawing the complex is not reformed, which means that the emulsion will break.

There is no absolute remedy for damage done to emulsions by extreme temperature changes, except to avoid or protect the emulsions from exposure to great heat or cold.

III. EXPERIMENTAL

The experimental section of this thesis is divided into the following sections: (1) purpose of investigation, (2) plan of investigation, (3) materials and equipment used, (4) method of procedure, (5) data and results, and (6) sample calculations.

Purpose of Investigation

The purpose of this investigation was: (1) to produce an oil-in-water emulsion, using a heavy white mineral oil (USP) and distilled water as the two immiscible liquids, (2) to employ ultrasonic energy generated by a piezoelectric crystal, (3) to evaluate the emulsion through the use of photomicrographs taken of each emulsion.

Plan of Investigation

The plan for this investigation was divided into three main sections: (1) literature review, (2) experimental, and (3) correlation of data.

Literature Review. The literature review of this investigation was conducted with two ideas in mind: (1) to review for the reader the theoretical and practical essentials of emulsions and emulsification required in this investigation, and (2) to show the effects that ultrasonic energy may have on emulsification.

Experimental. Oil-in-water emulsions were made, using a heavy paraffin oil and distilled water as the two immiscible liquids. A dye, Sudan IV, was added to the oil phase to aid in the identification of the dispersed phase and to give better contrast to the photomicrographs. Photomicrographs were taken of each emulsion for its evaluation. Ultrasonic energy was used to emulsify the two liquids. Results obtained were confirmed by multiple tests. A Waring blender was employed for selected comparative tests.

Correlation of Data. The data were analyzed by measuring the size of each particle in a 1-1/2-inch square section in the center of each photomicrograph. From this, a frequency distribution of the particle sizes was made for each emulsion. On the emulsions in which multiple data were taken, a variance analysis was performed to determine if

there was any systematic error in the data. Since the variance analysis shows no systematic error in the data, the "best value" was calculated for each set of data and a 95 per cent confidence limits was then assigned to these "best values" by making use of the "t" distribution.

Material

The following materials were used in this investigation. The specifications, the manufacturer, and the use of the material is listed.

Acetic Acid. A 28 per cent solution of acetic acid was prepared by procedure recommended in Kodak's Reference Handbook. Obtained from Eastman Kodak Company, Rochester 4, N. Y. Used as a stop bath in developing of photographic film and paper.

Adhesive. "Pliobond" an all purpose contact cement. Manufactured by W. J. Ruscoe Company, Akron 1, Ohio. Used to cement the aluminum collar of the special exposure chamber to the glass tubing.

Aluminum Tubing. 2-inch outside diameter, 1-1/2-inch inside diameter. Available from Aluminum Company of America, Alcoa Building, Pittsburgh 19, Penn. Used to make collar for special exposure chamber used with ultrasonic generator.

Brass Shim. Six-mils thickness, obtained from the stockroom of the Department of Chemical Engineering of the Missouri School of Mines and Metallurgy, Rolla, Missouri. Used as the diaphragm for the exposure chamber.

Dektol Developer. A Kodak developer for paper. Manufactured by Eastman Kodak Co., Rochester 4, N. Y. Used in the developing of prints.

Immersion Oil. Manufactured by Techni-Products Company, West Palm Beach Florida. Used as an immersion oil between the microscope slide and 97X objective lens.

Lens Paper. Obtained from Fisher Scientific Company, St. Louis, Missouri. Used for cleaning microscope lens.

Microdol Developer. A Kodak developer for film. Manufactured by Eastman Kodak Company, Rochester 4, N. Y. Used in the developing of film.

Oil, Paraffin. National Formulary, heavy, batch no. C-66047. Obtained from Amend Drug and Chemical Co., Inc., New York, N. Y. Used as the oil phase in emulsions prepared.

Petroleum Jelly. Obtained from the stockroom of the Department of Chemical Engineering of the Missouri School of Mines and Metallurgy, Rolla, Missouri. Used as a seal between microscope slide and the cover glass.

Photographic Film. Two types used. Kodak Panatomic-X and Plus-X film. Manufactured by Eastman Kodak Company, Rochester 4, N. Y. Used in taking photomicrographs of emulsions prepared.

Photographic Paper. Kodak Polycontrast, single weight photographic paper. Manufactured by Eastman Kodak Company, Rochester 4, N. Y. Used to print pictures of photomicrographs.

Rubber Gasket Material. Obtained from an old tire intertube found in the shop of the Chemical Engineering Building of the Missouri School of Mines and Metallurgy, Rolla,

Missouri. Used to make two gaskets for the exposure chamber constructed for use with the ultrasonic generator.

Sodium Oleate. Neutral Powder, lot no. 42750. Obtained from J. T. Baker Chemical Company, Phillipsburg, N. J. Used as emulsifying agent in the emulsions prepared.

Sodium Thiosulfate. Better known as hypo or acid fixer. Solution prepared as recommended in Kodak's Reference Manual. Obtained from Eastman Kodak Company, Rochester 4, N. Y. Used as an acid fixer in the developing of film and paper.

Sudan IV. Also known as Biebrich Scarlet Red. C. I. no. 258, total dye content 93 %, certification no. NZ 19. Manufactured by National Aniline Division of Allied Chemical and Dye Corporation, New York 6, N. Y. Used as a dye for the oil phase in the emulsions prepared.

Tubing, Glass. Pyrex tubing, forty-millimeters nominal outside diameter. Obtained from Fisher Scientific Company, Inc., St. Louis, Missouri. Used as the barrel of the exposure chamber.

Tygon Paint. Series TP81 clear, no. 617061, manufactured and distributed by the U. S. Stoneware Company. Used to adhere the sleeve of the exposure chamber to the Pyrex glass barrel.

Water, Distilled. Obtained from the distilled water tap, Unit Operation Laboratory Mezzanine, Room 105, Chemical Engineering Building, Missouri School of Mines and Metallurgy, Rolla, Missouri. Used as the water phase in the emulsions prepared.

Apparatus

The following items of apparatus were used in this investigation. The specification for use or purchase, the manufacturer or supplier, and use of apparatus are listed.

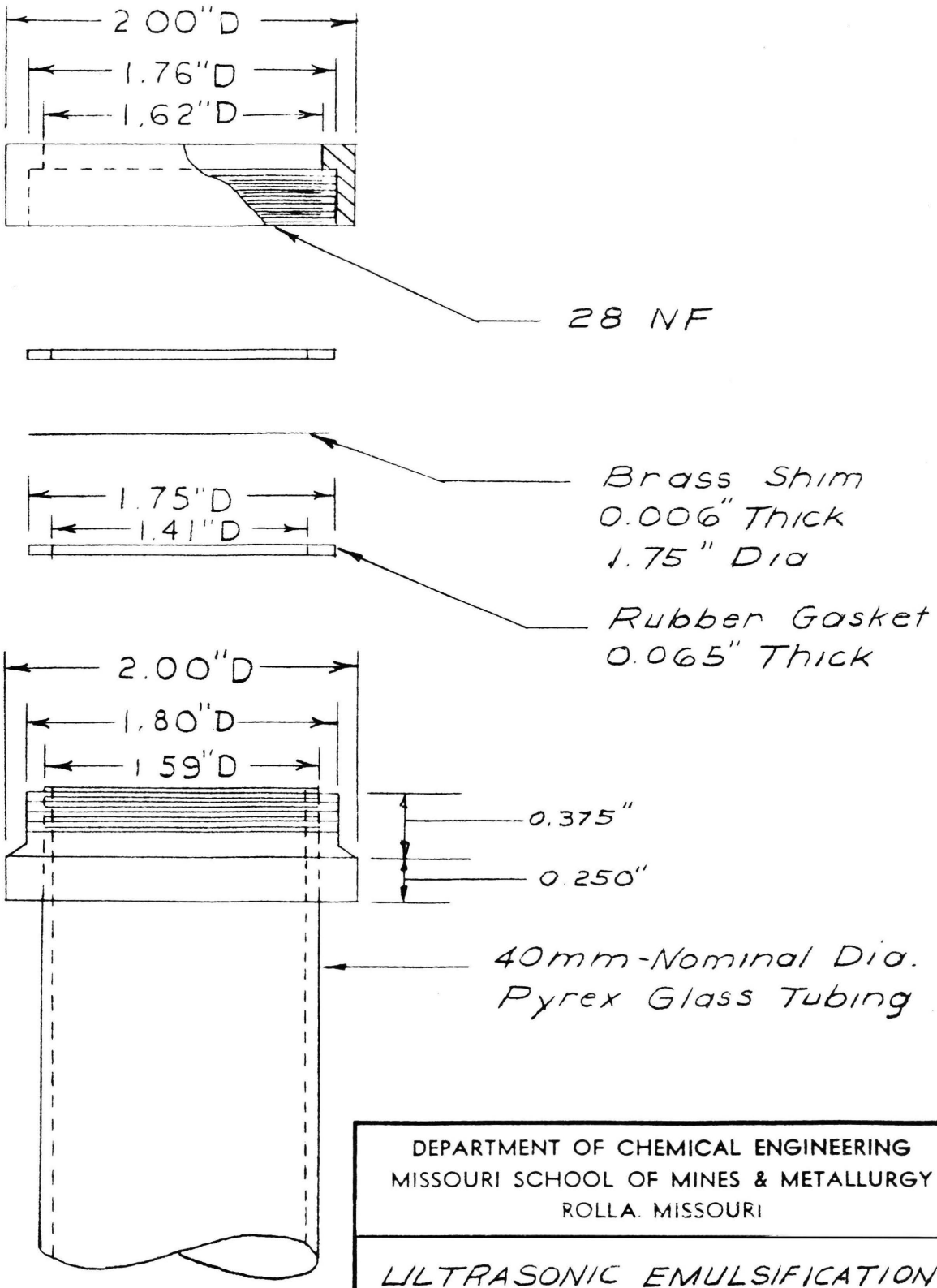
Bottles. Screw cap vials, 1/4-ounce, code no. 60910. Manufactured by Kimble Glass Company, Toledo 1, Ohio. Used to store emulsions.

Centrifuge, Micro. International, 110 volts, 60 cycles, 1780 RPM, no. 28569H. Manufactured by International Equipment Company, Boston, Mass. Used to test the stability of emulsions prepared.

Constant Voltage Transformer. Sola, 60 cycles, 1-phase, 95 to 125 primary volts, 115 secondary volts, 4.35 amperes, 500 rated V.A. Catalog no. 30808, series no. C27445. Manufactured by Sola Electric Company, Chicago, Ill. Used to provide a constant voltage to the ultrasonic generator.

Exposure Chamber. Special exposure chamber constructed out of Pyrex glass tubing, aluminum tubing, brass shim, and rubber gaskets. Specifications of this equipment are given in Figure 15. Used as an exposure chamber to emulsify the water and oil mixture with the GE Ultrasonic Generator.

Microscope. Spencer, Microstar trinocular microscope with integral illuminator base and variable transformer. Obtained from American Optical Company, St. Louis, Missouri. Used to examine emulsion samples and to take photomicrographs with the camera listed below. See Figure 16.



DEPARTMENT OF CHEMICAL ENGINEERING
MISSOURI SCHOOL OF MINES & METALLURGY
ROLLA, MISSOURI

ULTRASONIC EMULSIFICATION EXPOSURE CHAMBER

SCALE: Full	DATE	CASE NO:	490
DRAWN BY: JHR	1-17-59	FILE NO:	59
CHECKED BY: DJ.	1-17-59	FIGURE NO:	15
APPROVED BY: DJ.	1-17-59	SHEET NO:	1

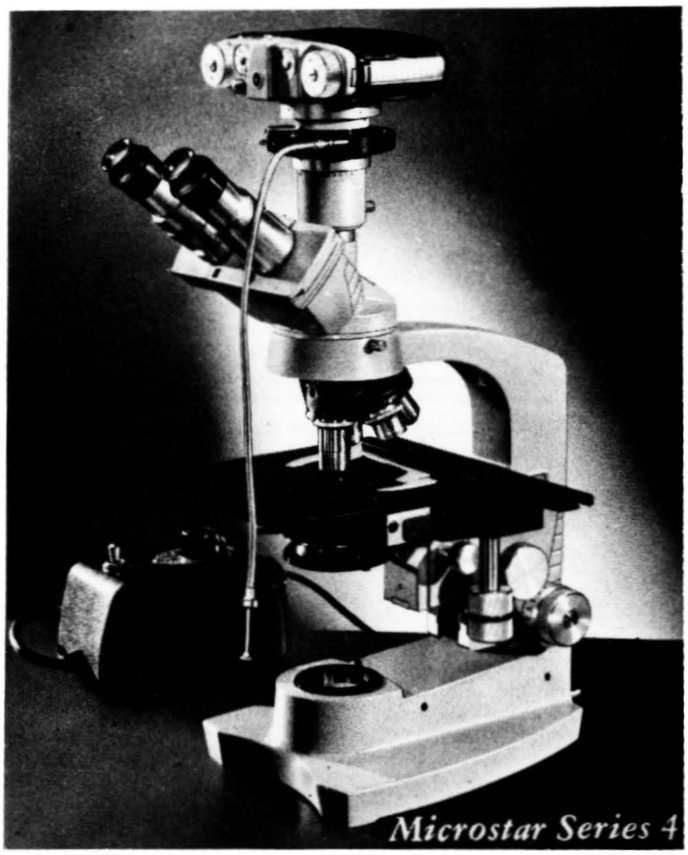


Figure 16. Microscope With Camera

Attached to Trinocular.

American Optical Instrument Division: "Microstar". p. 4. American Optical Instrument Division, Buffalo 15, New York.

Microscope Camera. 35-mm photomicrographic camera Model 635 for trinocular Microstar. Adapted by American Optical Company, Instrument Division, Buffalo 15, N. Y., from Kodak Pony 135 Model C, 24 x 36 mm transparency, 44-mm F/3.5 Kodak Anaston lens, 1, 5, 10, 25, 50, 125, "T", and "B" speeds. Manufactured by Eastman Kodak Company, Rochester 4, N. Y. Used to take photomicrographs.

Microscope Slides. Non-corrosive glass, 75 x 25 mm. Obtained from A. S. Aloe Company, St. Louis, Missouri. Used in conjunction with the microscope to observe and examine samples of emulsion.

Microscope Slide Cover Glass. Corning Glass Cover, non-corrosive optical brand glass, 22 mm square, 0.18 to 0.25 mm thick. Obtained from A. S. Aloe Company, St. Louis, Missouri. Used to cover the emulsion specimen that is being examined under the microscope to prevent evaporation of water phase and to make it possible to use the oil-immersion-lens.

Microscope Stage Micrometer. 75 x 25 mm glass slide with etched lines one-tenth and one-hundredth of a centimeter apart. Obtained from A. S. Aloe Scientific Company, St. Louis 12, Missouri. Used to measure the particle size of the oil droplets.

Oven. Precision, 220 volts, 60 cycles, 700 watts, 3.2 amperes. Series no. 16-1003, catalog no. 1474. Manufactur-

ed by Precision Scientific Company, Chicago, Ill. Used to determine the effect of heat on the stability on emulsions.

Photographic Equipment. The photographic equipment, located in the dark room, Room G-7, Chemical Engineering Building, Missouri School of Mines and Metallurgy, Rolla, Missouri, was used to develop and print all the photomicrographs.

Pipette, 10-ml. Ungraduated, volumetric pipette. Obtained from Fisher Scientific Company, St. Louis, Missouri. Used to measure and transfer both the oil and water to the exposure chamber.

Pipette, 5-ml. Graduated, volumetric pipette. Obtained from Fisher Scientific Company, St. Louis, Missouri. Used to measure and transfer both the oil and water to the exposure chamber.

Pipette, 2-ml. Graduated, volumetric pipette. Obtained from Fisher Scientific Company, St. Louis, Missouri. Used to measure and transfer both the oil and water to the exposure chamber.

Refrigerator. Westinghouse, Model M-9, Serial no. 6050848, 115 volts, 60 cycles, 3.2 amperes. Manufactured by Westinghouse Electric Corporation, Pittsburgh, Penn. Used to determine the effect of cooling on the stability on emulsions.

Spatula. Fisher, stainless steel, catalog no. 14-373. Obtained from Fisher Scientific Company, St. Louis, Missouri. Two of these were used to apply pressure to microscope cover glass to squeeze out the excess liquid.

Ultrasonic Generator. General Electric, catalog no. 8665966-G3, no. 3237515, 115 volts, 50/60 cycles, 300 kilocycles per second. Manufactured by General Electric Company, Schenectady, N. Y. Used as a source of ultrasonic energy. See Figure 17.

Volumetric Flasks. 1000 ml. glass stoppered, blue line exax, with T stopper. Obtained from Fisher Scientific Company, St. Louis, Missouri. Used to prepare stock solutions of 0.1, 0.2, 0.4 per cent sodium oleate.

Waring Blender. Waring, model 702, one speed, one-fourth horsepower motor, 115 volts, 60 cycles, 10,000 rpm. Manufactured by Waring Products Corporation, New York 36, N. Y. Used as a conventional source of energy in emulsification.

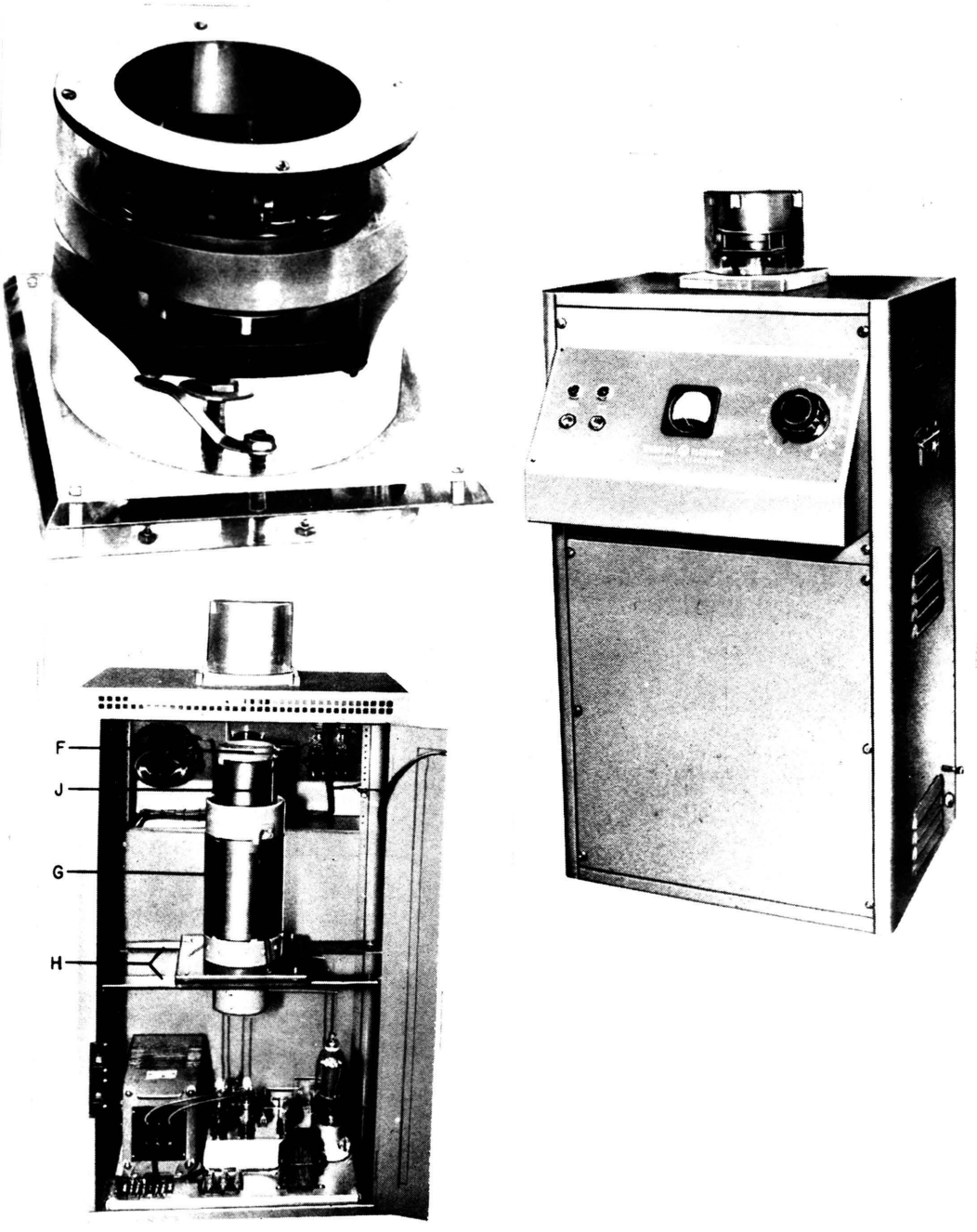


Figure 17. G. E. Ultrasonic Generator:
(a) Transducer Assembly, (b) Back Panel Open,
(c) Front View and Control Panel.

General Electric, "Instructions, Ultrasonic Generator Cat. No. 8665966G1, -G2, and -G3," p. 1 and 2. General Electric, Schenectady, N. Y.

Method of Procedure

The method of procedure for this investigation was divided into six general steps. They were: (1) construction of a suitable exposure chamber, (2) formulation, (3) emulsification, (4) testing the emulsion for stability, (5) taking photomicrographs of emulsions prepared, and (6) determination of particle size.

Construction of Exposure Chamber. The author was unable to find a test tube or similar piece of apparatus that would adequately serve the purpose of an exposure chamber for ultrasonic emulsification. Therefore, a special vessel was constructed. The wall of the exposure chamber was of glass tubing, and the bottom was an acoustical window.

The first attempt at making this exposure chamber consisted of sintering platinum (from a platinic chloride solution painted on the edge of pyrex glass tubing) into the glass in a flame. By this method a surface was prepared onto which a brass shim of 0.006-inch thickness was soldered. Because of the difficulty experienced in attempting to get the platinum to adhere uniformly to the surface of the glass, another method of making the exposure chamber was considered. The second approach to the problem, which perhaps was a better and simpler one, consisted of making a special collar out of aluminum tubing and adhering this to

the lower end of the glass tubing. The design and specification of this exposure chamber is shown in Figure 15.

Two exposure chambers were constructed. Pliobond contact cement was used to adhere the aluminum collar to the glass. Tygon paint (clear) served as the adhesive for the other chamber. The Pliobond cement was waterproof and apparently stable to the ultrasonic energy, but it possessed the undesirable property of plastic flow. The collar would move when pressure was applied to it causing a problem of leakage. The tygon paint served as an excellent adhesive since it was inert and formed a tough adhesive film especially when heat-dried.

Formulation. The first step in the formulation was to prepare 0.4, 0.2, and 0.1 per cent solutions of sodium oleate with distilled water as the solvent. The emulsifying agents were prepared and used in this manner to avoid the time-consuming job of weighing the powder on an analytical balance for each individual emulsion. Therefore, the amount of sodium oleate used in each emulsion is expressed in weight per cent of the water phase.

Next, a dye was added to the oil phase to aid in the identification of the oil phase under a microscope and to give a contrast to the photomicrographs taken of the emulsions. The dye selected was Sudan IV. Sudan IV is a bright red, water insoluble, organic dye. It was added to the oil by

weighing 0.0320 gram of the dye and dissolving it in one liter of paraffin oil.

The same procedure was used for each emulsion in adding the two phases to the exposure chamber. The water phase, with the proper amount of emulsifying agent dissolved in it, was measured with a graduated pipette and transferred to the exposure chamber. Next the proper amount of the paraffin oil, with the Sudan IV dye dissolved in it, was measured with a graduated pipette and added to the top of the water phase. No preliminary mixing was employed.

The amount of oil and water that was added depended on the oil-to-water ratio used. This ratio varied from 1:4 to 1:8 and to 1:16. The amount of emulsifying agent was utilized at three values: 0.1, 0.2, and 0.4 weight per cent sodium oleate, expressed in terms of the water phase.

Emulsification. Two different sources of mechanical energy were utilized for emulsification: (1) ultrasonics, and (2) Waring blender.

Emulsification by Ultrasonic Energy. A General Electric ultrasonic generator, with a piezoelectric crystal vibrating at a fixed frequency of 300 kilocycles per second, was used as the source of ultrasonic energy. The specially constructed exposure chamber was placed in the water bath and held rigid by means of a ring stand and clamps. The brass diaphragm bottom was placed 33.5 millimeters above the quartz crystal. After

the machine has been properly warmed up, according to the manufacturer instructions, the plate switch was turned on, permitting the power to be transmitted to the crystal. The power was increased until the reading of the D-C milliampere meter registered 175 milliamperes. The time of irradiation was varied between 2 and 4 minutes.

Emulsification by the Waring Blender. After the mixture had been placed in the chamber, the machine was turned on. The time of agitation was varied between 2 and 4 minutes, depending on the formula.

Stability Tests. Four separate tests on the stability were made on each of the emulsions produced. They were: (1) centrifuge test, (2) elevated temperature for one week at 55 °C, (3) refrigeration for one week at 5 °C, and (4) one week at ambient temperature.

Centrifuge Test. A two-milliliter graduated centrifuge tube was filled with the emulsion to be tested. This was placed in the centrifuge which had a speed of 1780 revolutions per minute. After 4, 8, 16, and 32 minutes, the amount of creaming and oil separation was recorded. If the emulsion was not broken after 32 minutes, a photomicrograph was taken of a sample from the cream layer.

Elevated Temperature Test. An eight-milliliter bottle was filled with the emulsion to be tested and

placed in an oven at 55 °C. The sample was left in the oven for a period of one week. During this time, the emulsions were examined once a day to notice if any of the emulsions had completely separated into two phases. After one week at 55 °C, the samples were removed from the oven, and the amount of creaming and oil separation was recorded. A photomicrograph was taken of a sample from the cream layer.

Low Temperature Test. A sample of each emulsion was placed in a refrigerator at 5 °C for one week. These samples were examined daily to see if any of the emulsions were completely separated into two phases. At the end of one week, the samples were removed from the refrigerator and examined. The amount of creaming and oil separation was then recorded. Also, a photomicrograph was taken of a sample from the cream layer.

Stability at Ambient Temperature. A sample of each emulsion was placed on a "shelf" for one week at ambient temperature in the research laboratory, Room 105 M-1, Chemical Engineering Building, Missouri School of Mines and Metallurgy, Rolla, Missouri. These samples were examined at the end of one week and the amount of creaming and oil separation was recorded. A photomicrograph of a sample from the cream layer was taken of each emulsion.

Photomicrograph. The same procedure was used throughout in the preparation of the microscope slides, prior to taking the photomicrograph. A 0.1-milliliter sample of the emulsion was diluted with 0.4 milliliter of distilled water. This was done to give a better picture of the particles, by cutting down on the number of particles that overlap each other, and therefore giving a more even distribution of the particles. A very small drop of the diluted emulsion was placed on a 3 x 1-inch glass microscope slide. To prevent the liquid from evaporating when examined under the microscope, and to make it possible to use the oil immersion lens, a cover glass was placed over the sample. The edges of the cover glass were coated with a thin layer of petroleum jelly before they were placed on the slide. The petroleum jelly served as a seal between the cover glass and the slide. Pressure was applied to the top of the cover glass with a pair of spatulas to force out the excess liquid. This gave a uniform layer of particles. Then a drop of immersion oil was placed on the cover glass and the slide was examined under the 97X objective lens. After a representative area was selected from the field, a picture was taken with the specially built camera, the trinocular of the microscope. The diaphragm of the camera was set wide open, and when panatomic-X film was used, the shutter speed was 1/25 second and 1/50 second for plus-X film. The lens condenser was 7/8 open and the voltage selector was set on 6.5 for all pictures.

Processing of Photographic Film and Paper. The standard procedure recommended in Kodak Reference Handbook was employed in developing and printing all films and papers.

Determination of Particle Size. The size of each particle was determined with the aid of a microscope stage micrometer. This stage micrometer was divided into 0.1 and 0.01 millimeter sections. A picture of this micrometer was taken under a microscope using the 97X objective. With the aid of this stage micrometer, the size of each particle in a 1-1/2 by 1-1/2 inch area in the center of each photograph was measured and recorded. See Figure 18. The total enlargement of the particle on the final print was approximately 960X.

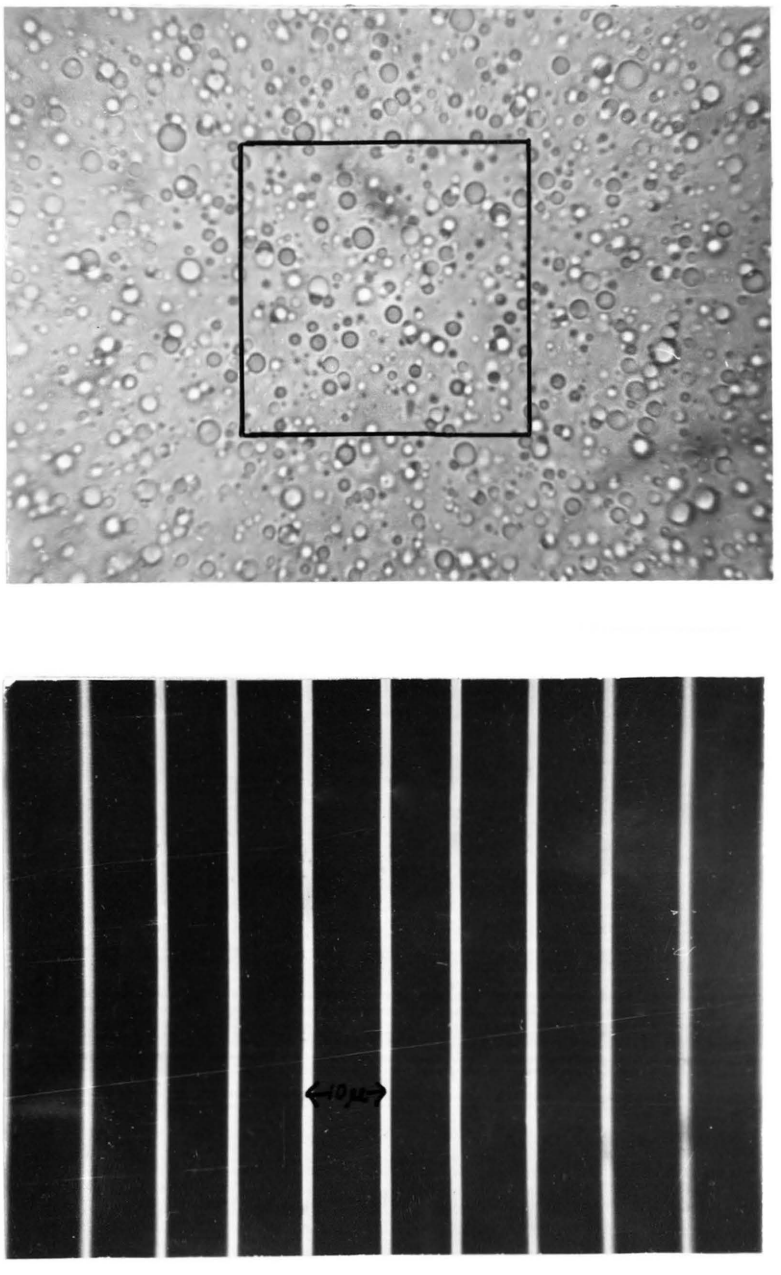


Figure 18. (a) Photomicrograph (690X) of Emulsion 59, With the 1-1/2-inch-square Section Outlined. (b) Stage Micrometer (690X).

Data and Results

Those data and results that were confirmed with multiple tests and subjected to statistical analysis will be considered here. Other data pertinent to this work but unconfirmed by multiple tests have been placed in an appendix of this thesis.

Particle Size Distribution. Tables III, IV, and V, show the data taken from emulsions having different oil-to-water ratio. Each of the emulsions listed in these tables contain 0.4 per cent of sodium oleate by weight in the water phase, were irradiated at a frequency of 300 kilocycles per second at a power output of 175 milliamperes for four minutes on the G.E. ultrasonic generator. Ten separate slides were prepared of each emulsion and one picture was taken of each slide. A 1-1/2-inch square section in the center of each photograph was outlined and the size and frequency of particles were measured and recorded. The results are shown in Tables III, IV, and V. The number of particles in each size range are expressed in per cent of the total number of particles in this 1-1/2-inch square section.

Weighted Means of Particle Size Distribution. A variance analysis of the data showed that the scattering in the data was not due to a systematic error. Therefore the "best value" with a 95 per cent confidence limits was calculated for each ratio. The results of these calculations are shown in Table VI.

TABLE III

Particle Size Distribution of Emulsions with 1:4 Oil-to-water Ratio Prepared on G.E. Ultrasonic Generator[a]

Emulsion Number	Picture Number	Size Distribution				
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %
58	9-1	61.4	34.0	4.6	0.0	0.0
	9-2	56.2	31.3	10.0	2.5	0.0
	9-3	50.5	35.2	12.4	1.9	0.0
	9-4	64.5	31.6	3.9	0.0	0.0
	9-5	67.3	24.3	5.6	2.8	0.0
	9-6	58.3	30.5	5.6	5.6	0.0
	9-7	65.0	31.4	3.6	0.0	0.0
	9-8	75.0	22.8	1.1	1.1	0.0
	9-9	40.0	51.0	9.0	0.0	0.0
	9-10	40.5	50.0	8.9	0.6	0.0
59	9-11	68.2	30.8	1.0	0.0	0.0
	9-12	55.9	41.4	2.7	0.0	0.0
	9-13	65.9	30.6	2.9	0.6	0.0
	9-14	39.5	47.9	12.0	0.6	0.0
	9-15	55.7	38.6	5.7	0.0	0.0
	9-16	61.4	36.6	2.0	0.0	0.0
	9-17	54.0	38.7	4.3	3.0	0.0
	9-18	68.3	26.2	5.5	0.0	0.0
	9-19	59.7	29.4	8.2	2.7	0.0
	9-20	71.2	27.9	0.9	0.0	0.0
60	9-21	55.4	38.2	5.7	0.7	0.0
	9-22	49.4	42.0	8.6	0.0	0.0
	9-23	56.3	38.4	3.3	1.3	0.0
	9-24	54.5	43.3	2.2	0.0	0.0
	9-25	57.3	36.2	5.9	0.6	0.0
	9-26	58.8	39.9	1.3	0.0	0.0
	9-27	47.4	39.2	12.2	1.2	0.0
	9-28	66.6	31.2	2.2	0.0	0.0
	9-29	43.0	52.4	4.6	0.0	0.0
	9-30	51.6	40.2	5.8	1.6	0.0

[a]Quartz crystal transducer, 300 Kilocycles, intensity held constant at a value corresponding to 175 milliamperes.

TABLE IV

Particle Size Distribution of Emulsions with 1:8 Oil-to-water Ratio Prepared on G.E. Ultrasonic Generator[a]

Emulsion Number	Picture Number	Size Distribution				
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %
55	7-1	55.4	23.1	10.8	9.2	1.5
	7-2	52.3	23.9	16.4	7.4	0.0
	7-3	53.0	30.6	12.2	2.1	2.1
	7-4	42.9	37.5	7.1	7.1	0.0
	7-5	59.2	22.4	10.2	6.1	2.1
	7-6	54.9	37.1	4.8	1.6	1.6
	7-7	47.8	31.8	13.6	4.5	2.3
	7-8	58.1	27.4	6.5	6.5	1.5
	7-9	38.8	32.7	10.2	12.2	6.1
	7-10	46.8	33.9	14.5	3.2	1.6
56	8-1	35.5	43.4	11.1	7.8	2.2
	8-2	45.9	25.9	14.1	9.4	4.7
	8-3	48.8	34.9	7.0	7.0	2.3
	8-4	60.0	26.6	6.7	0.0	6.7
	8-5	50.0	34.8	6.4	4.3	4.3
	8-6	41.2	36.8	17.6	2.9	1.5
	8-7	42.8	28.6	17.1	8.6	2.9
	8-8	21.4	45.7	20.0	8.6	4.3
	8-9	38.1	36.9	14.5	6.5	4.0
	8-10	48.6	31.9	12.5	5.6	1.4
57	8-11	51.5	38.2	7.3	1.5	1.5
	8-12	66.0	27.6	4.3	2.1	0.0
	8-13	34.0	39.6	9.4	17.0	0.0
	8-14	56.2	36.1	6.2	1.5	0.0
	8-15	53.4	37.8	4.4	4.4	0.0
	8-16	33.7	37.0	20.7	6.5	2.1
	8-17	49.4	29.8	10.4	7.8	2.6
	8-18	49.4	38.4	8.2	4.0	0.0
	8-19	50.4	36.2	11.8	1.6	0.0
	8-20	58.0	29.0	8.1	3.2	1.7

[a]Quartz crystal transducer, 300 Kilocycles, intensity held constant at a value corresponding to 175 milliamperes.

TABLE V

Particle Size Distribution of Emulsions with 1:16 Oil-to-water Ratio Prepared on G.E. Ultrasonic Generator[a]

Emulsion Number	Picture Number	Size Distribution				
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %
61	10-1	56.0	36.0	8.0	0.0	0.0
	10-2	36.1	52.8	11.1	0.0	0.0
	10-3	35.3	38.9	14.8	5.5	5.5
	10-4	53.0	29.4	17.6	0.0	0.0
	10-5	41.4	38.0	10.3	10.3	0.0
	10-6	40.6	34.4	21.9	3.1	0.0
	10-7	33.3	41.2	15.7	9.8	0.0
	10-8	40.0	40.0	6.7	6.7	6.6
	10-9	48.0	32.0	12.0	8.0	0.0
	10-10	34.4	43.8	12.5	9.3	0.0.
62	10-11	48.5	41.9	4.8	1.6	3.2
	10-12	44.7	39.5	13.2	2.6	0.0
	10-13	42.8	40.8	16.4	0.0	0.0
	10-14	44.7	46.1	9.2	0.0	0.0
	10-15	34.0	43.4	11.3	9.4	1.4
	10-16	42.2	48.9	6.7	2.2	0.0
	10-17	49.1	38.6	12.3	0.0	0.0
	10-18	39.9	48.9	8.2	3.0	0.0
	10-19	55.6	29.6	13.0	1.8	0.0
	10-20	45.2	41.5	12.2	1.1	0.0
63	10-21	37.1	42.8	17.2	2.9	0.0
	10-22	46.0	35.1	16.2	2.7	0.0
	10-23	29.7	42.2	17.2	7.8	3.1
	10-24	56.5	30.4	8.7	4.4	0.0
	10-25	54.2	41.7	0.0	4.1	0.0
	10-26	49.1	45.4	5.5	0.0	0.0
	10-27	54.1	29.7	10.8	5.4	0.0
	10-28	47.3	50.0	2.7	0.0	0.0
	10-29	45.4	32.8	7.3	5.4	9.1
	10-30	51.0	42.9	4.1	2.0	0.0

[a]Quartz crystal transducer, 300 Kilocycles, intensity held constant at a value corresponding to 175 milliamperes.

TABLE VI

Distribution of Particles in Per Cent Weighted Means

Particle Diameter, Microns	Particle Distribution: Oil-to-water Ratio 1:4 %	1:8 %	1:16 %
1	56.4 ± 3.2	50.5 ± 3.7	44.5 ± 3.4
2	38.0 ± 2.6	32.5 ± 2.1	40.2 ± 2.3
3	5.4 ± 1.3	10.2 ± 1.0	11.1 ± 1.6
4	0.6 ± 0.3	5.7 ± 1.8	3.3 ± 1.1
5-7	0.0	2.0 ± 0.2	0.7 ± 0.7

Figures 19, 20, and 21 show the results of these calculations in a graphical form. The points above and below each point through which the curve passes, are the extremes of the 95 per cent confidence limits. Figure 22 is a comparison of the "best value" for the 1:4, 1:8, and 1:16 oil-to-water ratio.

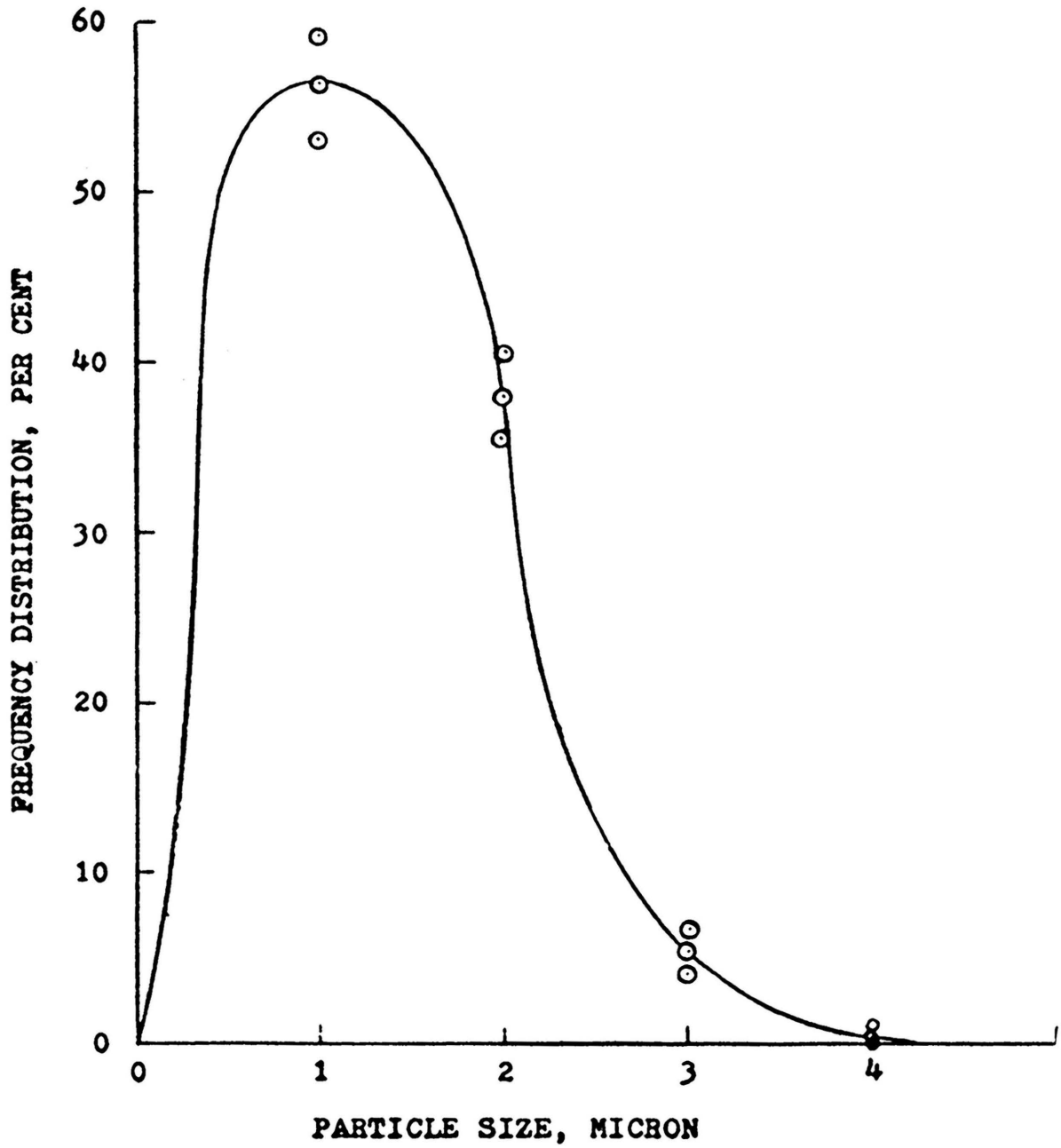


FIGURE 19. CURVE OF FREQUENCY DISTRIBUTION VERSUS PARTICLE SIZE FOR EMULSIONS WITH 1:4 OIL-TO-WATER RATIO, 0.4 % SODIUM OLEATE, AND IRRADIATED FOR 4 MINUTES WITH ULTRASONIC ENERGY AT A FREQUENCY OF 300 KILOCYCLES PER SECOND.

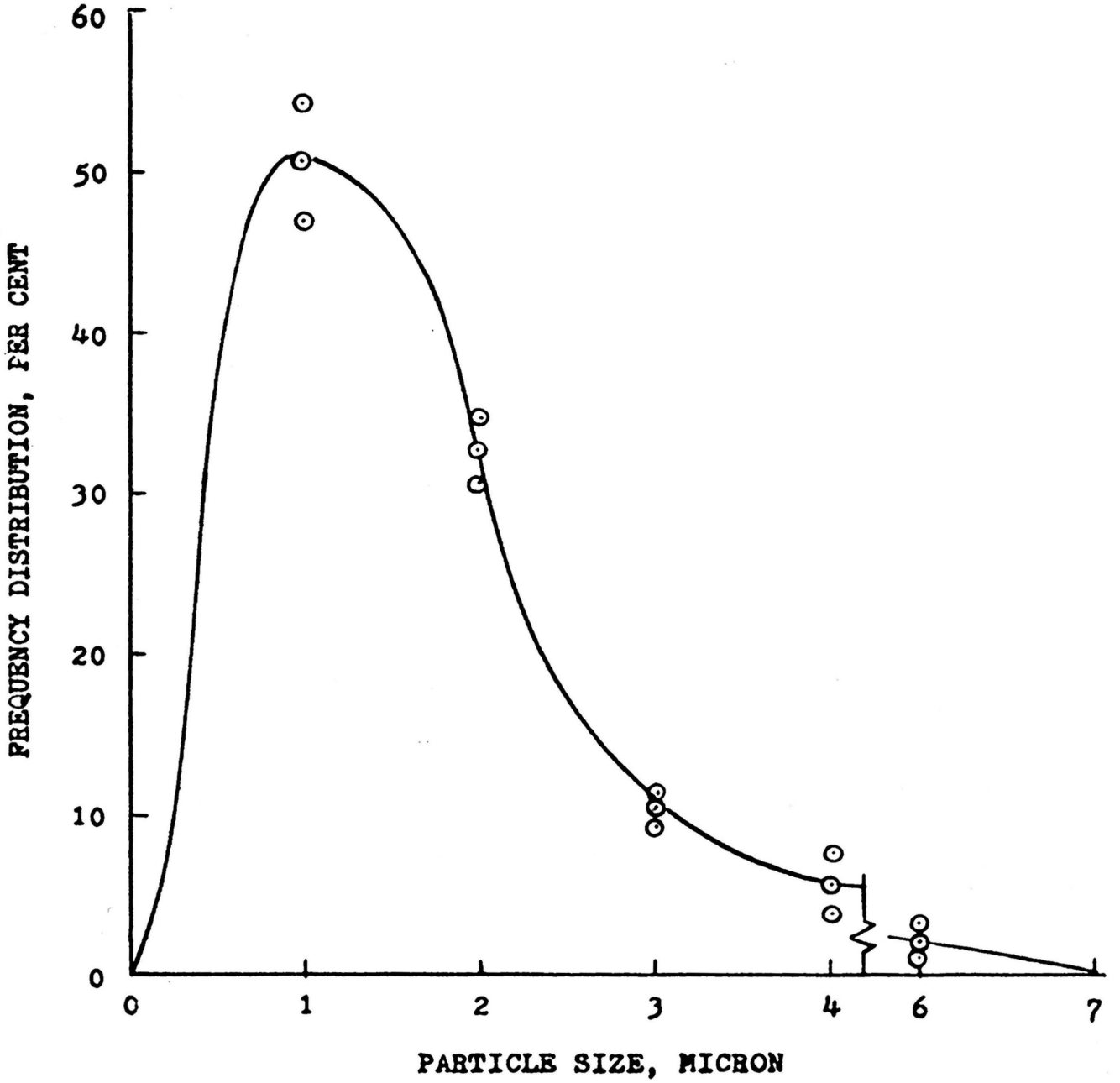


FIGURE 20. CURVE OF FREQUENCY DISTRIBUTION VERSUS PARTICLE SIZE FOR EMULSIONS WITH 1:8 OIL-TO-WATER RATIO, 0.4% SODIUM OLEATE, AND IRRADIATED FOR 4 MINUTES WITH ULTRASONIC ENERGY AT A FREQUENCY OF 300 KILOCYCLES PER SECOND.

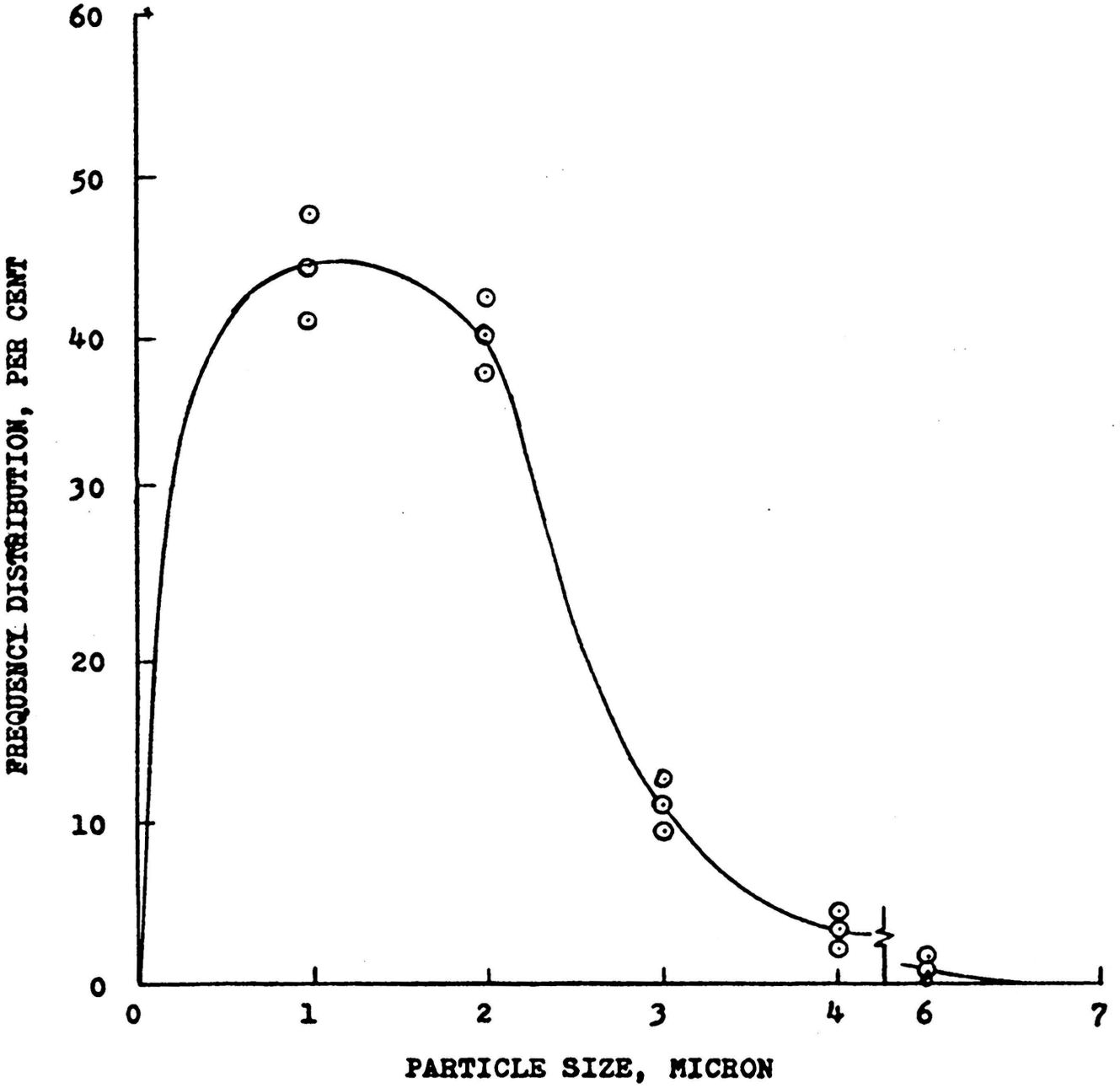


FIGURE 21. CURVE OF FREQUENCY DISTRIBUTION VERSUS PARTICLE SIZE FOR EMULSIONS WITH 1:16 OIL-TO-WATER RATIO, 0.4% SODIUM OLEATE, AND IRRADIATED FOR 4 MINUTES WITH ULTRASONIC ENERGY AT A FREQUENCY OF 300 KILOCYCLES PER SECOND.

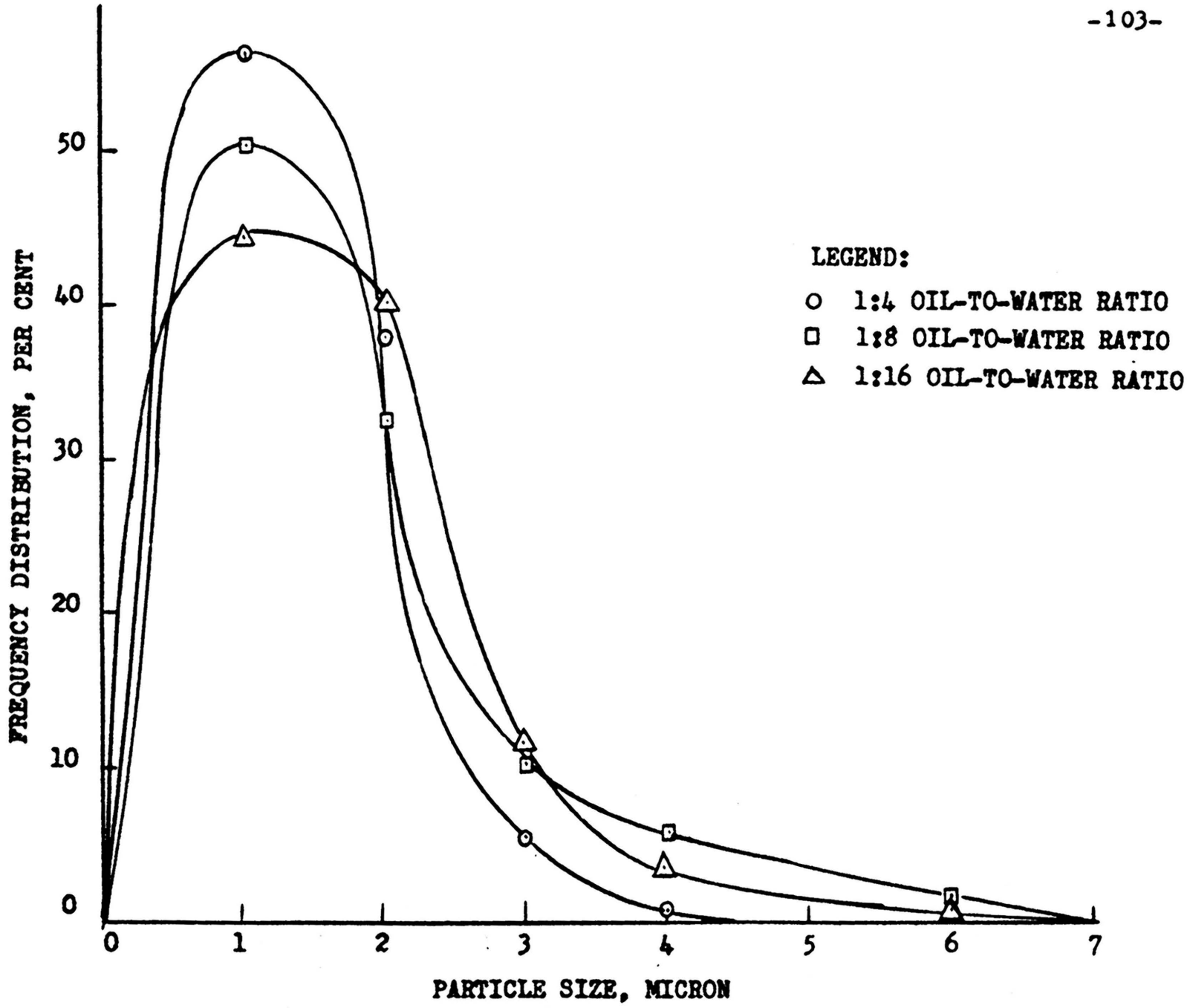


FIGURE 22. COMPARISON OF DISTRIBUTION CURVES FOR DIFFERENT OIL-TO-WATER RATIO

Sample Calculations

Examples of the different type calculations made in this investigation are presented in this section.

Variance Analysis. The "F" test that is outlined in Mickley, Sherwood, and Reed, "Applied Mathematics in Chemical Engineering" page 73, was employed for the variance analysis in this investigation. As an illustration, the per cent of particles in the one-micron range of emulsions 55 and 56 were used. The first step in this analysis was to substract 46 from each datum, and set up a table as illustrated in Table VII. This was done to give the data a value closer to zero, thereby making it easier to perform the necessary calculations. In the second step the columns (T_c) and the rows (T_r) were summed. The sum of T_r's should equal the sum of T_c's. Step three was to sum up the squares of all the individuals in the columns and the rows. The sum of the squares of the individuals in the columns should be equal to the sum of the square of the individuals in the row. See Table VII for steps one through three. Step four consists of squaring each T_c, summing and dividing by the number of rows (n_r). For this illustration step four would be:

$$\frac{(49.2)^2 + (-27.7)^2}{10} = 318.79 \qquad (6)$$

Step five, square T ($\Sigma T_c = T = \Sigma T_r$) and divide by $n_r n_c$, or

$$\frac{(21.5)^2}{(2)(10)} = 23.11 \qquad (7)$$

TABLE VII

Preliminary Tabulation of Data for "F" Test

Variance Analysis

Sample Number	Emulsion Number		T_r	ΣY^2
	55[a] %	56[a] %		
1	9.4	-10.5	-1.1	198.61
2	6.3	-0.1	6.2	39.70
3	7.0	2.8	9.8	56.84
4	-3.1	14.0	10.9	205.61
5	13.2	4.0	17.2	190.24
6	8.9	-4.8	4.1	102.25
7	1.8	-3.2	-1.4	13.48
8	12.1	-24.6	-12.5	751.57
9	-7.2	-7.9	-15.1	114.25
10	0.8	2.6	3.4	7.40
T_c	49.2	-27.7	21.5	
ΣX^2	642.24	1037.71		1679.95

Where:

T_r = sum of rows

T_c = sum of columns

ΣX^2 = sum of individual squares in each column

ΣY^2 = sum of individual squares in each row

[a]46 was substracted from each datum of emulsions 55 and 56.

Step six, set up a table similar to Table VIII. The sum of squares between columns was found by substracting step five from step four, (318.79 - 23.11 = 295.68). The sum of squares within the column was found by substracting step four from step three (1679.95 - 318.79 = 1361.16).

The degrees of freedom between the columns is one less than the number of columns. In this illustration the degree of freedom between the columns was 2 - 1 or 1. The degrees of freedom within the column is:

$$n_c n_r - n_c = (2)(10) - 2 = 18. \qquad (8)$$

where:

$n_c n_r$ = the number of columns times the number of rows.

n_c = the number of columns.

The population variance between the columns (σ^2 in the table) was found by dividing the sum of squares between the columns by the degree of freedom, or 295.68/1 = 295.68. The within sample or error variance (σ^2 within the column) was found by dividing the sum of the squares within the column by the degrees of freedom, or 1361.16/18 = 75.62. The value for "F" was found by dividing the population variance by the within sample or error variance, or 295.68/75.62 = 3.91. From a table on the distribution of "F" with 95 per cent confidence limits, the value of "F" was found to be 4.38. Since the calculated value of "F" was less than the value of "F" found in the table, the scattering in the above data was due to random errors and not to errors of method or bias.

TABLE VIII

Variance Analysis of Data in Table VII

Source of Variance	Sum of Squares	Degrees of Freedom	σ^2	"F"
Between Column	295.68	1	295.68	3.91
Within Column	1361.16	18	75.62	

Determination of the Weighted Means or Best Value. To illustrate the method used to determine the best value of the per cent of particles in a certain size range, the data from the 1-micron range of emulsions 58, 59, and 60 will be utilized. The method that is employed in this investigation is the same as the one illustrated in Mickley, Sherwood, and Reed, "Applied Mathematics in Chemical Engineering", page 69.

The first step is to calculate the average ($\bar{X}$) for each set of data. For emulsion 58, $\bar{X}$ was found to be 57.9; for emulsion 59, $\bar{X}$ was found to be 60.0; and for emulsion 60, $\bar{X}$ was found to be 54.0. The second step was to find the "sum of squares" which is defined as:

$$\Sigma(X - \bar{X})^2 = \Sigma(X^2) - (\Sigma X)^2/n \qquad (9)$$

where:

X = the individual datum

$\bar{X}$ = the average for a particular set of data

n = number of data.

The "sum of squares" for emulsion 58 was found to be 34,657.33 - 33,489.37 = 1,167.96; for emulsion 59 the "sum of squares" was found to be 790.08; and for emulsion 60 the "sum of squares" was found to be 391.66. The third step was to calculate the sample variance of the mean, S_m^2, which is defined as:

$$S_m^2 = \Sigma(X - \bar{X})^2/n(n - 1) \qquad (10)$$

where X, $\bar{X}$, and n are the same as those defined in equation 9.

For emulsion 58, S_m^2 was found to be 11.67.96/(10)(9) = 12.98; for emulsion 59, S_m^2 was found to be 790.08/(10)(9) = 8.78; and for emulsion 60, S_m^2 was found to be 391.66/(10)(9) = 4.35. After these values were found, the best value of the three sets of data was calculated from the following equation:

$$\bar{X}_{b.v.} = \frac{\bar{X}_1/S^2_{m,1} + \bar{X}_2/S^2_{m,2} + \bar{X}_3/S^2_{m,3}}{1/S^2_{m,1} + 1/S^2_{m,2} + 1/S^2_{m,3}} \qquad (11)$$

where:

$\bar{X}_{b.v.}$ = the best value of the averages of the individual sets of data

$\bar{X}$ = the average for the individual sets of data

S_m^2 = the sample variance of the mean as defined in equation 10.

Using the above equation, the best value ($\bar{X}_{b.v.}$) was found to be 56.4.

The next step is to calculate the confidence limits that can be assigned to the best value. In order to do this, the sample variance of the best value is needed which is defined as:

$$S^2_{m,b.v.} = \frac{1}{1/S^2_{m,1} + 1/S^2_{m,2} + 1/S^2_{m,3}} \qquad (12)$$

where:

$S^2_{m,b.v.}$ = the best value of the sample variance of the mean

S_m^2 = the sample variance of the mean of the individual sets of data.

Using the above equation, the best value of the sample variance, $S^2_{m,b.v.}$, was found to be 2.38. The 95 per cent confidence limits can be found from a table on distribution of "t" in any statistic book. Since there are 30 data points and three means ($\overline{X}_1$, $\overline{X}_2$, and $\overline{X}_3$), the degrees of freedom is 30 - 3 or 27. The "t" limits for 27 degrees of freedom is $\pm$ 2.05. Therefore, the 95 per cent confidence limits on the best value is $\pm$ 2.05$(2.38)^{\frac{1}{2}}$ or $\pm$ 3.16.

The best value for the per cent of particles in the one-micron range for an emulsion with an oil-in-water ratio of 1:4 (0.4 per cent of sodium oleate in the water phase, and irradiated with ultrasonic energy at a frequency of 300 kilocycles per second at a power output of 175 milliamperes for four minutes) was found to be 56.4 $\pm$ 3.2.

IV DISCUSSION

The discussion is presented in three sections: (1) discussion of results, (2) recommendations, and (3) limitations.

Discussion of Results

The discussion of results includes a discussion of the data and results of this investigation, as well as a discussion of the method of procedure.

Significance of the Analysis of Variance. The analysis of variance that was performed in the sample calculations, is known as the "F" test. The "F" test is based upon the following considerations: in a single set of data, two types of errors are possible, i.e., random errors and errors of method or bias. The statistics "F" is the ratio of the variance which contains both random and method errors to the variance which includes random errors only. If the calculated values of "F" are greater than the probability values that are tabulated in various statistics books, it means the error is due to method or bias and is not random. In the analysis of variance that was illustrated in the sample calculations, the calculated value of "F" (3.91) was smaller than the corresponding probability value that was found in the table (4.38). This means that in less than 5 per cent of the cases could

the observed difference in sample mean be explained on the method that was used to obtain the observed data.

The analysis of variance was performed only on the per cent of particles in the one-micron range. This test was not performed on the number of particles in the 2, 3, 4, and 5 to 7 microns range. It is fairly obvious that if there is a random scattering of data in the one micron range, there will also be a random scattering in the other ranges. It should be pointed out that this analysis was not performed on the results obtained from emulsions with an oil-to-water ratio of 1:4 and 1:16. Since it was fairly obvious from the variance analysis performed on the emulsions with an oil-to-water ratio of 1:8, that the scattering was a random scattering, this same reasoning would apply to the results of the emulsions with an oil-to-water ratio of 1:4 and 1:16. Therefore, only one analysis of variance was made.

Best Value. The method utilized to determine the best value for each ratio is illustrated in the sample calculations. This method can be used only when the difference in means between two or more sets of data is due to random factors, and not due to errors of method or bias. The 95 per cent confidence limits that was assigned to the best value means that 95 times out of a 100 the true population mean will fall within these limits. In the example illustrated in the sample calculations, the best value ($\bar{X}_{b.v.}$) was found to be 56.4 with a 95 per cent confidence limits of $\pm$ 3.2. An alternative

interpretation of this result is that only 5 times in 100 will the analyst be in error if he assigns the limits 56.4 ± 3.2 to his results.

The use of 95 per cent confidence limits is arbitrary. Narrower limits could have been chosen which would decrease the degrees of probability to the results. Also, broader limits could have been selected which would give the results a higher degree of probability. The 95 per cent confidence limits were the limits that were most widely used and this was the reason why the author choose to use it.

Sampling of Emulsions for Photomicrograph. There is a possibility that the procedure used in choosing a sample of an emulsion to be photomicrographed could have an effect on the data. A pipette was used to select a sample from the emulsion before preparing the microscope slide as is explained in the method of procedure. In drawing a sample from the emulsion, it is possible that there was an unusually heavy concentration of larger particles (3 to 5 microns range) in comparison to the rest of the emulsion at this particular point. This would tend to give a flatter distribution curve. On the other hand, the opposite effect is possible, that is, there could have been a heavy concentration of particles in the 1-micron range at the point of sampling. This would give a steeper distribution curve.

The same thing is also true in taking photomicrographs of the emulsions. The photomicrograph represents a very

small area of the microscope slide. Therefore there is a possibility that the picture that was taken was not the best representation of the slide.

Comparison of 1:4, 1:8, and 1:16 Oil-to-water Ratio. Figures 19, 20, and 21 are distribution curves of emulsions made on the GE ultrasonic transducer at a frequency of 300 kilocycles per second, and agitated for 4 minutes with an output of 175 milliamperes with the following ratio: 1:4, 1:8, and 1:16 respectfully. The curves are drawn through the points representing the best value of each ratio. The points above and below the best values are the extremes of the confidence limits that were calculated for each best value.

Figure 22, shows a group of three curves plotted on the same axis. This graph shows that the 1:4 oil-to-water ratio gave the best results. This was followed by 1:8 and then by the 1:16 oil-to-water ratio. Time did not permit the author to obtain data on an 1:2 or 1:3 oil-to-water ratio to see if it would follow the same pattern.

It will be noted from the graph that there are no particles larger than 4 microns in the emulsion with an oil-to-water ratio of 1:4. Whereas in the 1:8 and 1:16 ratio, particles were found to be as large as 7 microns.

Random Scattering of Data. The author was not aware of the fact that there was a random scattering of results until after most of the experimental work was completed. The re-

sults were not analyzed immediately because of the photographic work involved. This was done for several reasons. A roll of photographic film used in this investigation usually contained 36 exposures. Because it is inconvenient and time consumming to develop short strips of film (between 4 and 10 exposures) the author exposed the whole roll of film before developing the film. Also, to insure that the same enlargement was used in printing pictures of the photomicrographs, the author waited until several rolls of film were developed before printing the pictures. Upon analyzing these results and preparing a number of series of preliminary graphs, it was found that the data did not follow consistent patterns. Duplicate experiments were then performed. It was found that results could not always be duplicated. This lead the investigator to set up a statistical approach to the problem.

GE Ultrasonic Generator vs. Waring Blender. Examination of the data in the appendix shows that the particle size of the emulsions made with ultrasonic generator had a larger per cent of the particles in the one and two-micron range than those made with the Waring blender. Those emulsions made with the waring blender had more oil droplets in the 5 to 10-micron range and usually had the largest particle size than an identical emulsion that was made with ultrasonic energy. From these data, there is reason to believe that emulsions with a finer and more uniform dispersion can be made with ultrasonic energy than by mechanical energy such as the Waring blender.

It should be pointed out that there is not enough data in the appendix to make a statistical analysis to verify the above statement. However, in the possibility that these data may be of consequence in an extension of this work, they are included.

Stability Tests. Data that were taken on the stability of the emulsions are included in the appendix for reasons discussed above. After examining the data on the various stability tests, there is reason to believe that the emulsions made with ultrasonic energy exhibit greater stability than those made by the Waring blender.

Creaming. The amount of creaming was measured at the end of each stability test. These data are recorded in the notebook, but are not included in this thesis, because they are empirical and cannot be used as a quantitative basis to determine what is the best ratio.

Centrifuge Test. The purpose of the centrifuge test was to record the time it would take to break the emulsions. The centrifuge that was used in this investigation had a speed of 1780 revolutions per minute. The centrifugal force developed at this speed expressed in terms of "G's" is approximately 180 "G's". This was not great enough to break most of the emulsions into two separate phases within 32 minutes, indicating that most of the emulsions were fairly stable.

Counting of Particles. A photomicrograph was taken of each emulsion and after each stability test. An area 1-1/2 by 1-1/2 inches was outlined in the center of each photomicrograph and the size of each particle was measured. At the high magnification (97X) of the oil-immersion objective of the microscope the center portion of the photomicrograph was in sharp focus and the outer edges were less clearly defined. For this reason the central portion of the photograph was used in determining the particle size distribution.

Preparation of Microscope Slide. In preparing the microscope slide, the emulsion to be photographed was diluted with distilled water. This was done to cut down on the number of particles thereby making it easier to count and measure the size of each particle.

Ultrasonic Emulsification. The work reported in the literature by past investigators most dealt with the phenomenon of emulsification and the feasibility of using ultrasonic energy for this purpose. Many investigators reported the effect of using different frequencies. Some studied the effects of different variables such as, temperature, emulsifying agent, time of exposure, and intensity. Very few investigators made a comparison between ultrasonic and mechanical energy. In 1949, Campbell and Long[64] made the following statement in their report: "The emulsions produced by ultrasonic irradiation appear to have somewhat smaller particle sizes and slightly better stability than those formed

by mechanical means." This statement is in agreement with the overall observations of the author in this investigation. The author was unable to find a record of anyone who had investigated the effects of ultrasonic energy with respect to the oil-to-water ratio.

Recommendation

There are numerous ways in which this investigation could be extended and improved. Each recommendation will be discussed under their appropriate headings.

Microscope Camera. A camera which will automatically cock the shutter when the film is wound would be an improvement over the present camera that is attached to the microscope. This would prevent an unintentional double exposure. Another improvement over the present camera would be one with a film counter that will automatically return to zero when a new roll of film is loaded in the camera. This would be an aid in keeping the record correct on the number of exposures that have been taken.

Height of Exposure Chamber above the Piezoelectric Crystal. An extention of this investigation would be to investigate the effect that the height of the exposure chamber above the quartz crystal on the GE ultrasonic generator would have on the particle size distribution of the emulsion. This could be done by accurately measuring the

distance between the diaphragm of the exposure chamber and the crystal with some type of micrometer.

Jet-edge Ultrasonic Generator. Another way to improve this investigation would be to obtain a jet-edge ultrasonic generator and investigate the effect this type of ultrasonic energy will have on emulsification. The jet-edge generator has one advantage over the piezoelectric crystal in that they can be more easily adapted for commercial work.

Frequency. The frequency used in this investigation was fixed at 300 kilocycles per second. To study the effect of using a higher or lower frequency would be interesting and would be of great value to future investigators.

Intensity. The intensity used in this investigation was held constant by keeping the power to the quartz crystal constant at 175 milliamperes. The use of a vacuum tube voltmeter with a special probe to measure this acoustical intensity would improve this investigation. Also, the effect of varying the intensity should be investigated.

Temperature. When ultrasonic energy is transmitted through a liquid medium, some of the energy is absorbed by the medium and converted into thermal energy. Therefore, it may be desirable to control the temperature of the mixture during emulsification. Another possible extention of this problem would be to investigate in greater detail the effect of temperature on emulsification.

Other Types of Emulsions. Another extention to the work done in this investigation would be to make other types of emulsions. Water-in-oil emulsions should be studied as well as oil-in-water. Various types of emulsifying agents should be used. Emulsions with an oil-to-water ratio of 1:2 and 1:3 should be made and compared with data on the graph in Figure 22.

Colloid Mill. It is the belief of the author that a colloid mill such as the Gaulin mill will produce a better emulsion than a Waring blender. Therefore a colloid mill should be used to produce emulsions for comparison with the emulsions prepared by ultrasonic energy.

Economic Cost. No attempt was made to determine if the use of ultrasonic energy in emulsification would be economically feasible. Future work along this line should prove to be quite a challenge.

Limitations

The work done in this investigation was governed by the following limitations.

Frequency. The frequency of the ultrasonic waves used in this investigation was fixed, 300 kilocycles.

Intensity. The intensity of the ultrasonic energy was measured in terms of the current supplied to the piezoelectric crystal. The same intensity was used throughout this investigation. This intensity was held constant by holding the current to the piezoelectric crystal constant at 175 milliamperes.

Oil-to-water Ratio. The following oil-to-water ratio were used: 1:4, 1:8, and 1:16.

Type of Emulsion. Oil-in-water emulsions were made in this investigation.

Emulsifying Agent. Sodium oleate was the emulsifying agent that was used. The following amounts of sodium oleate were used: 0.1, 0.2, and 0.4 per cent, expressed in weight per cent of the water phase.

Time of Emulsification. Two and four minutes were the times used for emulsification.

Objective Lens of the Microscope. The 97X objective lens was used in conjunction with the camera to examine and photograph all emulsions.

V. CONCLUSIONS

The emulsification of a clear, heavy, paraffin oil, N.F., in distilled water containing 0.4 per cent of sodium oleate by means of the GE ultrasonic generator operating at a frequency of 300 kilocycles per second, with a power output to the piezoelectric crystal corresponding to 175 milliamperes and irradiated for 4 minutes led to the following conclusions:

1. The 1:4 oil-to-water emulsion had 11.9 per cent more particles in the one-micron range, based on the height of the ordinate of the curves, than the 1:8 oil-to-water ratio, and 27.1 per cent more than the 1:16 ratio.

2. The 1:8 oil-to-water emulsion had 13.5 per cent more particles in the one-micron range, based on the height of the ordinate of the curves, than the 1:16 oil-to-water ratio.

VI SUMMARY

The utilization of ultrasonic energy for emulsification is, in some respects, a unique method for making emulsions. In the past 10 to 15 years many investigators have investigated the feasibility of using this type of energy.

The purpose of this investigation was to evaluate the feasibility of employing ultrasonic energy for emulsification. This was done by taking photomicrographs of the emulsions and using these photomicrographs as an aid in this evaluation. A Waring blender was also used to make similar emulsions for comparison purposes.

Oil-in-water emulsions were made using a heavy white mineral oil and distilled water as the two immiscible liquids. Sodium oleate was the emulsifying agent for this investigation. After each emulsion was made, a series of ten photomicrographs were taken of each emulsion. The size of each particle in a 1-1/2-inch square section in the center of the photomicrograph was recorded, and a particle size distribution made.

A variance analysis was performed on the data collected. This analysis showed that there was a random scattering in the data. Since the scattering was not due to a systematic error, the best value for the per cent of particles in the

1-, 2-, 3-, 4-, and 5-7-micron range was calculated for each individual oil-to-water ratio.

This investigation gave some evidence that ultrasonic energy will produce a better emulsion than an identical emulsion made by mechanical means.

Three oil-to-water ratios were made with ultrasonic energy at a frequency of 300 kilocycles and an intensity corresponding to 175 milliamperes. The 1:4 oil-to-water ratio was found to have a larger per cent of its particles in the one-micron range than the 1:8 and 1:16 ratio. The 1:8 ratio was found to have a larger per cent of its particles in the one-micron range than the 1:16 ratio.

VII. APPENDIX

The data in Tables IX to XVIII of this appendix were not confirmed by multiple tests and therefore could not be subjected to statistical analysis. Since they are pertinent to this investigation and in the possibility that these data may be of consequence in an extension of this work, they are included in this appendix.

TABLE IX

Particle Size Distribution of Emulsions Prepared on G.E. Ultrasonic Generator[a]

TABLE IX

Particle Size Distribution of Emulsions Prepared on G.E. Ultrasonic Generator[a]

Emulsion Number	Oil-to-water Ratio	Emulsifying Agent,[b] %	Emulsifying Time, Min.	Picture Number	1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-11-μ, %
1	1:4	0.1	4	1-2	17.5	50.7	20.6	8.0	1.6	1.6
2	1:4	0.1	4	1-2	57.0	25.0	13.0	2.0	3.0	0.0
3	1:4	0.1	2	1-4	30.0	38.7	17.5	11.2	1.3	1.3
5	1:4	0.05	8	1-5	37.5	40.6	15.6	4.7	1.6	0.0
6	1:4	0.05	4	1-6	39.4	36.4	15.1	6.1	3.0	0.0
10	1:2	0.2	4	1-8	45.0	45.0	5.0	4.0	1.0	0.0
11	1:2	0.2	8	1-9	45.0	39.6	12.7	0.9	1.8	0.0
12	1:2	0.2	4	1-10	33.6	43.7	16.4	3.6	2.7	0.0
13	1:4	0.2	4	1-12	41.5	42.3	11.2	4.2	0.8	0.0
14	1:4	0.4	2	1-14	32.4	44.1	20.6	2.9	0.0	0.0
15	1:2	0.4	4	1-16	26.0	47.4	17.4	6.9	2.3	0.0
34	1:8	0.1	4	2-23	16.3	54.5	23.3	3.5	2.3	0.0
35	1:8	0.1	4	2-24	31.8	49.1	17.5	1.6	0.0	0.0
36a	1:8	0.1	2	4-28	13.0	34.8	27.5	7.3	17.4	0.0
37a	1:8	0.2	4	4-29	21.5	52.9	20.7	3.3	1.6	0.0
38	1:8	0.4	4	2-27	40.5	46.4	10.7	1.2	1.2	0.0
39	1:8	0.4	2	3-5	29.1	51.6	9.7	3.2	6.4	0.0
40	1:16	0.1	4	3-6	42.5	48.2	7.5	1.8	0.0	0.0
42	1:16	0.2	4	3-20	26.5	36.7	24.5	10.2	2.1	0.0
43	1:16	0.2	2	3-21	20.0	33.3	26.7	6.7	13.3	0.0
46	1:4	0.1	4	6-7	36.5	51.7	9.4	1.2	1.2	0.0
47	1:8	0.2	4	6-8	68.8	26.9	4.3	0.0	0.0	0.0
48	1:16	0.2	4	6-9	56.8	39.2	2.0	1.0	1.0	0.0
49	1:4	0.2	4	6-10	52.8	28.8	10.0	6.4	1.6	0.0
50	1:4	0.2	4	6-11	60.4	32.9	6.0	0.7	0.0	0.0
51	1:16	0.4	4	6-12	78.2	21.8	0.0	0.0	0.0	0.0
52	1:16	0.4	4	6-13	78.4	20.8	0.8	0.0	0.0	0.0
53	1:4	0.4	4	6-14	71.4	24.6	2.0	2.0	0.0	0.0
54	1:4	0.4	4	6-15	74.7	21.9	1.7	1.1	0.6	0.0

[a]Quartz crystal transducer, 300 kilocycles, intensity held constant at a value corresponding to 175 milliamperes.

[b]Sodium Oleate was used as an emulsifying agent. Per cent sodium oleate is expressed in weight per cent of the water phase.

TABLE X

Particle Size Distribution of Emulsions Prepared on G.E. Ultrasonic Generator[a] After 1 Week at Ambient Temperature

Emulsion Number	Picture Number	1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-11-μ, %
10	1-27	36.1	45.8	9.7	3.6	4.8	0.0
11	1-28	22.6	50.5	17.2	9.7	0.0	0.0
12	1-29	22.2	48.2	14.9	8.6	4.9	1.2
13	1-30	26.0	44.0	19.0	9.0	2.0	0.0
14	1-31	26.6	51.1	13.5	5.5	3.3	0.0
15	1-32	9.4	34.4	26.1	21.8	8.3	0.0
34	5-1	41.9	40.1	10.7	5.5	1.8	0.0
35	5-2	50.0	39.1	8.5	1.8	0.6	0.0
38	5-5	60.1	36.5	3.4	0.0	0.0	0.0
39	5-16	15.4	56.1	15.3	8.8	3.3	1.1
40	5-17	47.5	41.8	9.8	0.9	0.0	0.0
41	5-18	34.2	29.3	21.9	12.2	2.4	0.0
42	5-25	45.1	43.9	8.6	2.4	0.0	0.0
43	5-26	8.5	38.2	25.5	12.8	10.8	4.2
44	5-27	54.7	41.8	3.5	0.0	0.0	0.0
45	5-28	28.4	45.9	13.5	12.2	0.0	0.0

[a]Quartz crystal transducer, 300 kilocycles per second, intensity held constant at a value corresponding to 175 milliamperes.

TABLE XI

Particle Size of Emulsions Prepared on G.E. Ultrasonic Generator[a] After 32 Minutes in Centrifuge

Emulsion Number	Picture Number	Size Distribution					
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-11-μ, %
2	1-7	19.1	66.4	10.0	3.4	1.1	0.0
10	1-11	34.0	40.4	15.0	7.4	3.2	0.0
13	1-17	31.3	48.5	9.2	5.5	4.7	0.8
14	1-18	11.3	42.2	26.8	14.5	5.2	0.0
36a	4-30	16.3	27.3	20.0	20.0	14.6	1.8
37a	4-31	11.1	62.5	19.4	4.9	2.1	0.0
38	3-7	26.5	46.4	20.5	6.6	0.0	0.0
39	3-8	13.9	41.8	19.0	16.4	8.9	0.0
40	3-22	43.7	50.0	3.9	1.6	0.8	0.0
41	3-23	0.0	18.0	34.0	21.0	12.0	15.0
42	3-24	29.6	43.5	17.7	8.3	0.9	0.0
43	3-25	24.4	37.2	24.4	9.2	2.5	2.5
44	4-12	34.3	56.4	6.4	2.9	0.0	0.0
45	4-13	21.5	47.1	21.5	7.1	2.8	0.0

[a]Quartz crystal transducer, 300 kilocycles per second, intensity held constant at a value corresponding to 175 milliamperes.

TABLE XII

Particle Size of Emulsions Prepared on G.E. Ultrasonic Generator[a] After 1 Week at 5°C

Emulsion Number	Picture Number	Size Distribution					
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-11-μ, %
34	5-6	41	49	10	0.0	0.0	0.0
35	5-7	38.5	41.5	12.6	5.2	2.2	0.0
38	5-10	48.5	38.1	12.4	1.0	0.0	0.0
39	5-19	26.8	41.2	11.3	9.4	11.3	0.0
40	5-20	56.0	35.5	7.8	0.7	0.0	0.0
41	5-21	34.0	44.0	16.0	4.0	0.0	2.0
42	5-29	30.5	52.9	12.5	3.3	0.0	0.8
43	5-30	34.6	42.3	9.7	7.7	3.8	1.9
44	5-31	17.4	79.0	3.6	0.0	0.0	0.0
45	5-32	38.1	23.8	15.9	17.4	4.8	0.0

[a]Quartz crystal transducer, 300 kilocycles per second, intensity held constant at a value corresponding to 175 milliamperes.

TABLE XIII

Particle Size of Emulsion Prepared on G.E. Ultrasonic Generator[a] After 1 Week at 55°C

Emulsion Number	Picture Number	Size Distribution					
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-11-μ, %
1	1-19	48.5	39.5	6.1	2.2	3.7	0.0
2	1-20	24.5	45.1	16.7	9.8	3.9	0.0
10	1-21	33.3	44.9	13.8	6.9	1.1	0.0
11	1-22	35.8	46.4	16.7	1.1	0.0	0.0
12	1-23	30.6	44.9	12.2	8.2	4.1	0.0
13	1-24	29.0	44.0	23.0	3.0	1.0	0.0
14	1-25	30.7	48.9	14.7	3.4	2.3	0.0
15	1-26	41.3	42.9	11.0	4.0	0.8	0.0
34	5-11	53.5	37.4	8.0	1.1	0.0	0.0
35	5-12	24.4	53.5	15.0	5.5	1.6	0.0
38	5-15	23.4	65.7	8.8	2.1	0.0	0.0
39	5-22	13.1	38.1	19.7	12.0	15.8	1.3
40	5-23	33.1	52.7	12.0	2.2	0.0	0.0
41	5-24	6.6	33.4	26.6	33.4	0.0	0.0
42	5-33	29.0	54.1	13.7	2.7	0.5	0.0
43	5-34	40.9	50.0	9.1	0.0	0.0	0.0
44	5-35	51.9	45.6	2.5	0.0	0.0	0.0
45	5-36	23.7	50.5	19.6	5.2	1.0	0.0

[a]Quartz crystal transducer, 300 kilocycles per second, intensity held constant at a value corresponding to 175 milliamperes.

TABLE XIV

Particle Size Distribution of Emulsions Prepared on Waring Blender

Emulsion Number	Oil-to-water Ratio	Emulsifying Agent,[a] %	Emulsifying Time, Min.	Picture Number	1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-11-μ, %
17	1:4	0.1	4	1-33	22.5	28.2	23.9	15.5	7.0	2.9
18	1:4	0.1	2	1-34	19.6	49.0	19.6	7.8	4.0	0.0
19	1:4	0.1	2	1-35	15.4	23.1	27.0	11.5	11.5	11.5
20	1:4	0.05	4	1-36	77.0	13.2	4.4	4.4	1.0	0.0
21	1:4	0.05	8	2-2	24.4	46.3	12.2	9.8	4.9	2.4
23	1:4	0.2	4	2-4	31.8	36.4	18.2	4.5	9.1	0.0
24	1:4	0.2	4	2-5	34.9	36.1	14.0	9.3	5.7	0.0
25	1:4	0.4	2	2-7	25.0	39.3	17.8	10.7	3.6	3.6
26	1:8	0.2	2	2-8	13.6	31.8	36.4	9.1	4.6	0.0
27	1:8	0.2	4	2-9	22.7	51.5	12.1	9.1	4.6	0.0
28	1:8	0.4	4	2-10	17.2	34.5	25.9	10.3	10.3	1.8
29	1:8	0.1	4	2-11	17.2	31.1	22.4	15.5	12.1	1.6
30	1:16	0.2	2	2-17	29.6	31.5	20.4	16.7	1.8	0.0
31	1:16	0.1	2	2-18	13.3	30.0	20,0	10.0	16.7	10.0
32	1:16	0.05	2	2-21	19.4	48.4	16.1	9.7	3.2	3.2
33	1:16	0.05	4	2-22	11.1	29.6	29.6	18.5	7.4	3.8

[a]Sodium oleate was used as an emulsifying agent. Per cent sodium oleate is expressed in weight per cent of the water phase.

TABLE XV

Particle Size Distribution of Emulsions Prepared on Waring Blender After 1 Week at Ambient Temperature

Emulsion Number	Picture Number	Size Distribution						
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-10-μ, %	11-15-μ, %
17	3-16	11.1	27.0	19.0	19.0	17.5	6.4	0.0
18	3-17	19.0	54.0	16.0	9.0	0.0	2.0	0.0
19	3-18	3.8	38.5	23.1	7.7	15.4	11.5	0.0
23	3-19	19.0	38.1	27.0	12.7	1.6	0.0	1.6
24	3-26	3.1	15.4	33.9	33.9	12.2	1.5	0.0
25	3-27	47.3	26.3	18.5	6.6	1.3	0.0	0.0
26	4-2	13.4	50.5	20.6	8.3	4.1	3.1	0.0
27	4-3	34.7	33.7	21.1	7.4	3.1	0.0	0.0
28	4-4	11.0	33.0	30.0	22.0	4.0	0.0	0.0
29	4-5	19.1	37.3	18.2	20.0	5.4	0.0	0.0
30	4-20	26.9	44.8	17.9	6.0	4.4	0.0	0.0
31	4-21	32.2	37.9	13.8	8.1	4.6	2.3	1.1
32	4-22	46.9	47.6	4.8	0.7	0.0	0.0	0.0
33	4-23	29.2	56.2	10.1	4.5	0.0	0.0	0.0

TABLE XVI

Particle Size Distribution of Emulsions Prepared on Waring Blender After 32 Minutes in Centrifuge

Emulsion Number	Picture Number	Size Distribution						
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-10-μ, %	11-15-μ, %
19	2-3	13.4	29.9	23.9	22.4	8.9	1.5	0.0
23	2-6	30.5	31.9	18.8	10.1	7.2	0.0	1.5
24	2-12	7.2	40.2	30.9	14.4	7.3	0.0	0.0
25	2-13	7.7	15.4	15.4	23.1	23.1	7.7	7.6
27	2-14	28.4	52.8	12.1	5.5	1.2	0.0	0.0
28	2-15	30.6	31.6	17.2	18.4	2.2	0.0	0.0
29	2-16	10.8	42.8	17.8	19.1	8.3	1.2	0.0
30	2-19	15.3	47.2	20.8	12.5	2.8	1.4	0.0
31	2-20	30.0	37.2	15.7	11.4	5.7	0.0	0.0

TABLE XVII

Particle Size Distribution of Emulsions Prepared by Waring Blender After 1 Week at 5°C

Emulsion Number	Picture Number	Size Distribution						
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-10-μ, %	11-15-μ, %
17	3-12	3.0	23.9	34.4	22.4	16.3	0.0	0.0
18	3-13	19.2	53.9	19.2	4.8	1.9	1.0	0.0
19	3-14	0.0	20.0	0.0	20.0	28.0	16.0	0.0
23	3-15	14.5	32.3	14.5	12.9	6.4	3.2	1.6
24	4-14	12.0	41.0	25.0	13.0	8.0	1.0	0.0
25	4-15	22.2	33.3	16.7	8.3	11.1	2.8	5.6
26	4-16	31.0	34.5	13.8	3.5	6.9	6.9	3.4
27	4-17	22.3	41.5	24.5	9.6	2.1	0.0	0.0
29	4-19	22.0	43.0	19.0	10.0	6.0	0.0	0.0
30	4-24	43.9	31.8	10.6	9.2	4.5	0.0	0.0
31	4-25	24.3	37.8	16.2	13.5	6.9	1.3	0.0
32	4-26	21.4	57.1	17.1	4.4	0.0	0.0	0.0
33	4-27	27.6	51.1	11.7	5.4	2.1	2.1	0.0

TABLE XVIII

Particle Size Distribution of Emulsions Prepared by Waring Blender After 1 Week at 55°C

Emulsion Number	Picture Number	Size Distribution						
		1-μ, %	2-μ, %	3-μ, %	4-μ, %	5-7-μ, %	8-11-μ, %	11-15-μ, %
17	3-9	4.5	22.4	37.3	26.9	8.9	0.0	0.0
18	3-10	8.9	43.3	25.4	14.9	6.0	1.5	0.0
23	3-11	11.4	48.6	11.4	17.2	5.7	5.7	0.0
24	4-6	5.3	30.3	25.0	23.7	13.1	2.6	0.0
25	4-7	4.5	31.8	22.8	18.2	18.2	0.0	0.0
26	4-8	18.2	45.4	18.2	18.2	0.0	0.0	0.0
27	4-9	12.6	41.8	32.9	7.6	5.1	0.0	0.0
28	4-10	37.2	45.1	11.8	2.0	3.9	0.0	0.0
29	4-11	22.4	41.5	18.1	9.6	7.4	1.0	0.0
30	4-32	17.1	37.2	30.0	12.9	2.8	0.0	0.0
31	4-33	14.8	35.2	22.2	16.7	9.3	1.8	0.0
32	4-34	23.5	26.5	14.7	23.5	8.8	3.0	0.0
33	4-35	18.0	51.7	19.2	6.7	4.4	0.0	0.0

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Addenda

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